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The annual subscription is £3. Those desiring to become Fellows of the Society should apply for further information to the Secretaries, Burlington House, London, W.1.

CL.—*A Theory of Colour on the Basis of Molecular Strain. The Effect of Chromophoric Superposition.*

By SIKHIBHUSHAN DUTT.

THE visible colour of substances is due to selective absorption of certain of the electro-magnetic vibrations causing the sensation of white light and the transmission of the remainder. In the present paper an attempt is made to show that selective absorption is due to molecular strain, such strain being imparted to the molecule by the distortion of the normal valency directions produced by any of the following causes :

(*a*) Formation of a double or triple bond.
(*b*) Formation of a cyclic from an open-chain compound.
(*c*) Unequal distribution of the masses attached to the atom.

The amount of strain is roughly proportional to the angular displacements of the valency directions of the atoms.

Strain in a molecule can be intensified by loading, the greatest effect being obtained when the load is in close proximity to the centre of strain. The farther the load is from this centre, the less is its effect.

The effect produced when two sources of strain are in close proximity in a molecule is much greater than that produced when they are remote from each other, because in the former case the intervening single linking also assumes a comparatively strained condition, thereby increasing the total rigidity of the molecule. The two strains produce the greatest effect when they originate in the same atom ; they have scarcely any mutual effect, each operating independently of the other, when they are situated at atoms separated by more than one single linking.

The position of the absorption maximum of a dye, the molecule of which contains two different and distantly situated chromophores, is approximately the mean of the positions of the maxima of the two components of the dye, each containing one chromophore. For example, the absorption maximum of the dye

$$NMe_2 \cdot C_6H_4 \cdot N{:}N \cdot C_6H_4 \cdot C(C_6H_4 \cdot NMe_2){:}C_6H_4{:}NMe_2$$

is at λ 5570, and those of its components, benzeneazodimethylaniline and malachite-green, are at λ 5040 and λ 6190 respectively (mean, λ 5615). A dye containing several chromophores of the same kind has almost the same absorption maximum as the dye containing only one such chromophore. Hence, in each of these two cases, the effects of the strains, situated in distant positions in the molecule, are independent of each other.

Experimental.

Azotriphenylmethane Dyes. Series I. Dyes containing One or Two Azo-groups attached to One Benzene Nucleus.

These dyes were obtained by oxidising the leuco-bases formed by condensing mono- and bis-azobenzaldehydes with dimethylaniline.

Preparation of Azobenzaldehydes.—The following mono- and bis-azobenzaldehydes were prepared by diazotising the substance named first in the bracket and coupling the product with the second-named substance. *p*-Aminobenzaldehyde was diazotised as described in D.R.-P. 85233 of 1895, and *m*-aminobenzaldehyde in concentrated hydrochloric acid. The coupling with phenol was done in 10% sodium hydroxide solution. The coupling with aniline or dimethylaniline was done in a mixture of concentrated hydrochloric and glacial acetic acids, which were thereafter gradually neutralised with sodium carbonate.

Monoazobenzaldehydes: (1) Benzeneazobenzaldehyde, $PhN{:}N{\cdot}C_6H_4{\cdot}CHO(p)$, prepared by the method described in Beilstein's "Organische Chemie," Vol. IV, p. 1068. (2) *p*-Hydroxybenzeneazobenzaldehyde, $(p)OH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CHO(p)$ (*p*-aminobenzaldehyde; phenol). (3) *p*-Dimethylaminobenzeneazobenzaldehyde, $(p)NMe_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CHO(p)$ (*p*-aminobenzaldehyde; dimethylaniline). (4) *p*-Aminobenzeneazobenzaldehyde, $(p)NH_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CHO(p)$ (*p*-aminobenzaldehyde; aniline). (5) *p*-Hydroxybenzeneazo-*m*-benzaldehyde, $(p)OH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CHO(m)$ (*m*-aminobenzaldehyde; phenol). (6) *p*-Dimethylaminobenzeneazo-*m*-benzaldehyde, $(p)NMe_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CHO(m)$ (*m*-aminobenzaldehyde; dimethylaniline). (7) *p*-Aminobenzeneazo-*m*-benzaldehyde, $(p)NH_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CHO(m)$ (*m*-aminobenzaldehyde; aniline). (8) Benzeneazosalicylaldehyde, $PhN{:}N{\cdot}C_6H_3(OH)(p){\cdot}CHO(m)$ (aniline; salicylaldehyde). This substance is identical with the compound prepared by Borsche (*Ber.*, 1900, **33**, 1325) from benzeneazophenol, chloroform, and sodium hydroxide. (9) *p*-Hydroxybenzeneazosalicylaldehyde, $(p)OH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_3(OH)(p){\cdot}CHO(m)$ (*p*-aminophenol hydrochloride; salicylaldehyde). (10) *p*-Methoxybenzeneazobenzaldehyde, $(p)OMe{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CHO(p)$, prepared by treating (2) with methyl sulphate and 3% sodium hydroxide solution. (11) 2:4-Dihydroxybenzeneazobenzaldehyde, $C_6H_3(OH)_2{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CHO(p)$ (*p*-aminobenzaldehyde; resorcinol). (12) 2:3:4-Trihydroxybenzeneazobenzaldehyde, $C_6H_2(OH)_3{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CHO(p)$ (*p*-aminobenz-

aldehyde; pyrogallol). Bisazobenzaldehydes: (13) *p*-Hydroxybenzeneazobenzeneazobenzaldehyde,

$$(p)OH\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot CHO(p)$$

(No. 4, diazotised as described in D.R.-P. 85233; phenol). (14) *p*-Dimethylaminobenzeneazobenzeneazobenzaldehyde,

$$(p)NMe_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot CHO(p)$$

(No. 4; dimethylaniline). (15) *p*-Hydroxybenzeneazobenzeneazo-*m*-benzaldehyde, $(p)OH\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot CHO(m)$ (No. 7, diazotised in concentrated hydrochloric acid; phenol). (16) *p*-Dimethylaminobenzeneazobenzeneazo-*m*-benzaldehyde,

$$(p)NMe_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot CHO(m)$$

(No. 7; dimethylaniline).

No diazoamino-compound was formed in the preparation of substances 4 and 7.

Substances 2, 11, 12, and 13 were crystallised from glacial acetic acid, and substances 3—8, 10, and 14—16 from alcohol. Substance 9 separated in an amorphous form from acetic acid.

Some properties of the azo-aldehydes are given in Table I.

TABLE I.

Azobenzaldehydes.

Azo-aldehyde.	Appearance.	M. p.	N % (theor. % in brackets).
2	Golden-yellow spangles with metallic lustre.	199°	12·5 (12·3)
3	Glistening, red prisms.	170	16·9 (16·6)
4	Yellowish-brown prisms.	158	18·5 (18·7)
5	Orange-yellow prisms.	164—165	12·2 (12·3)
6	Brownish-yellow needles.	116	16·8 (16·6)
7	Yellow prisms.	85—87	18·3 (18·7)
8	Golden-yellow needles.	128	12·1 (12·3)
9	Dark brown powder.	117—120	11·9 (11·6)
10	Bright yellow needles.	130—131	11·4 (11·7)
11	Microscopic, red needles.	Above 300	11·2 (11·6)
12	Microscopic, brown needles.	,,	11·1 (10·8)
13	Glistening, brownish-yellow needles.	190	17·3 (16·9)
14	Dark red needles.	142—143	19·2 (19·6)
15	Glistening orange-yellow prisms.	135	16·7 (16·9)
16	,, ,, ,,	128—129	19·8 (19·6)

General Method of Condensation of Azobenzaldehydes with Dimethylaniline, and Preparation of the Corresponding Azotriphenylmethane Dyes.—A solution or suspension of the azobenzaldehyde (1 mol.) and dimethylaniline (2 mols.) in ten times their volume of a mixture of equal parts of concentrated hydrochloric and glacial acetic acids was heated under reflux for periods of time varying from 3 to 12 hours, the end of the reaction being shown by the production of a clear solution and the change in colour from dark red to pale yellow.

The solution was poured into water, made alkaline with sodium carbonate, and every trace of dimethylaniline removed by distillation in steam. The white precipitate of the leuco-base was dissolved in dilute hydrochloric acid and reprecipitated from the filtered solution with sodium carbonate. In most cases the leuco-base could not be further purified or crystallised, owing to oxidation, and was therefore directly oxidised to the dye.

The oxidation was carried out by heating a solution of the leuco-base in sufficient 50% acetic acid with slightly more than the theoretical quantity of freshly precipitated and moist manganese dioxide (prepared by quantitative precipitation of potassium permanganate in warm water with alcohol) on the steam-bath for about 1 hour, with frequent stirring. After filtration, the solution of the colouring matter was treated with excess of saturated sodium acetate solution, and the precipitated dye was washed with water, dried, and crystallised from various solvents such as chloroform–ligroin, benzene, acetic acid, alcohol, and acetone, chloroform–ligroin (1 : 2) being the best solvent for the purpose. The substances thus obtained were acetates of the corresponding carbinol bases, and crystallised in glistening prisms or leaflets with a coppery lustre. They are generally sparingly soluble in water or benzene, moderately easily soluble in dilute mineral acids, alcohol, acetone, or acetic acid, very soluble in chloroform or pyridine, and insoluble in ligroin. They dye wool in various shades, from reddish-violet to deep blue.

Series II. Azotriphenylmethane Dyes containing Two Azo-groups attached to Two Benzene Nuclei.

Dyes of this series were prepared by tetrazotising *pp'*-diaminotriphenylmethane and its substitution products, coupling the products with dimethylaniline (2 mols.) in the usual manner, and oxidising the leuco-bases thus formed.

1. *pp'-Diaminotriphenylmethane*, $CHPh(C_6H_4{\cdot}NH_2)_2$, was obtained by O. Fischer's method (*Annalen*, 1881, **206**, 147).

2. p-*Hydroxy*-p'p''-*diaminotriphenylmethane*,

$$OH{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NH_2)_2.$$

—An intimate mixture of *p*-hydroxybenzylideneaniline (1 mol.), aniline hydrochloride (1 mol.), and concentrated hydrochloric acid (5 mols.) was heated in a sealed tube for 6 hours. The product was diluted with water, filtered, and the filtrate rendered alkaline with sodium carbonate solution. The resulting white precipitate, after being washed with water, crystallised from pyridine–alcohol in colourless needles, not melting at 295°. It dissolved very easily in dilute acids to pale yellow solutions, and was found to contain

two amino-groups by titration with $N/2$-sodium nitrite (Found: N, 9·3. $C_{19}H_{18}ON_2$ requires N, 9·7%).

3. p-*Dimethylamino*-p′p″-*diaminotriphenylmethane*,

$$NMe_2{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NH_2)_2.$$

—*p*-Dimethylaminobenzaldehyde (5 g.), aniline (7 g.), and strong hydrochloric acid (50 c.c.) were boiled under reflux for about 5 hours. The leuco-base was isolated as in the above instance. It crystallised from alcohol in colourless leaflets, m. p. 152°. It was very soluble in dilute acids and was found to contain two amino-groups by the standard method (Found: N, 13·6. $C_{21}H_{23}N_3$ requires N, 13·2%).

General Method of Preparation of the Dyes of this Series.—The diaminotriphenylmethane (1 mol.) in excess of dilute hydrochloric acid was treated with sodium nitrite (2 mols.), and the tetrazo-solution added to dimethylaniline (2 mols.) dissolved in strong hydrochloric or glacial acetic acid. On gradual neutralisation of the acid with sodium carbonate, the azo-dye separated. After being washed and crystallised from alcohol or glacial acetic acid, the leuco-base in hot glacial acetic acid was oxidised to the carbinol by freshly precipitated manganese dioxide in the usual manner. The dyes thus obtained are yellow, but the leuco-bases are brown. They dissolve in concentrated hydrochloric acid with a pink colour, whilst in ordinary solvents the colour is yellow.

Series III. Azotriphenylmethane Dyes containing Three Azo-groups attached to Three Benzene Nuclei.

These dyes were obtained by tetrazotising *p*-benzeneazo-*p′p″*-diaminotriphenylmethane and its substituted derivatives, and coupling the products with dimethylaniline in the usual way. The leuco-bases thus obtained are unaffected by oxidation. In behaviour they are all similar to simple azo-dyes like benzeneazodimethylaniline. They are all yellow, but dissolve in concentrated hydrochloric acid with a red colour.

1. p-*Benzeneazo*-p′p″-*diaminotriphenylmethane*,

$$PhN{:}N{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NH_2)_2.$$

—This substance was obtained by heating benzeneazobenzaldehyde (1 mol.) with aniline (2 mols.) and concentrated hydrochloric acid (10 mols.) in a sealed tube at 200° for 6 hours. It crystallises from alcohol in brownish-yellow needles, m. p. 174°, and is very easily soluble in dilute acids (Found: N, 14·5. $C_{25}H_{22}N_4$ requires N, 14·8%).

2. p-4-*Dimethylaminobenzeneazo*-p′p″-*diaminotriphenylmethane*,

$$NMe_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NH_2)_2.$$

—*p*-Dimethylaminobenzeneazobenzaldehyde (6 g.), 5 g. of aniline,

30 c.c. of strong hydrochloric acid, and 20 c.c. of glacial acetic acid were heated under reflux for about 3 hours until the colour of the solution had changed from dark crimson to pale yellow. The solution was poured into water and made alkaline with sodium carbonate; the precipitate produced, after being filtered off, washed and dried, crystallised from benzene in brownish-yellow needles, m. p. 165° (Found: N, 17·0. $C_{27}H_{27}N_5$ requires N, 16·6%).

3. p-4-*Hydroxybenzeneazo*-p′p″-*diaminotriphenylmethane*,

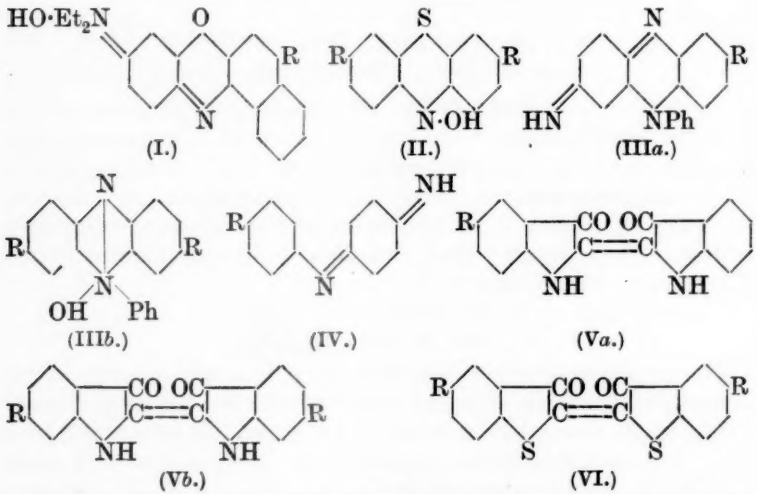
$$OH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}NH_2)_2.$$

—This substance was prepared from *p*-hydroxybenzeneazobenzaldehyde (1 mol.) and aniline (2 mols.) in a similar way to the above. It crystallised from alcohol in yellow aggregates, m. p. 162—163° (Found: N, 14·5. $C_{25}H_{22}ON_4$ requires N, 14·2%).

Series IV. Dyes containing Different Kinds of Chromophores.

For the preparation of the following dyes of the mixed type, all the diazotisations or tetrazotisations were carried out in cold strong sulphuric acid solution with the theoretical quantities of sodium nitrite. The sulphuric acid solutions were then diluted with ice-water and coupled with the required quantities of dimethylaniline in the usual manner:

Formula (R = ·N:N–C$_6$H$_4$–NMe$_2$).



(1) Azo-oxazine dye: *Nile-blue*-2-*azodimethylaniline* (formula I), from diazotised Nile-blue A; dark violet, microscopic needles from chloroform–benzene (N found, 15·4; theo., 14·9%).

(2) Azo-thiazine dye: *Lauth's violet*-2 : 7-*bisazodimethylaniline*

(II), from tetrazotised Lauth's violet; brownish-yellow powder from pyridine (N found, 19·7; theo., 19·2%).

(3) Azo-safranine dyes: (*a*) *Safranine-2-azodimethylaniline* (III*a*), from diazotised phenosafranine hydrochloride; dark violet needles from alcohol (N found, 20·4; theo., 20·1%). (*b*) *Safranine-2 : 7-bisazodimethylaniline* (III*b*), from tetrazotised phenosafranine hydrochloride; brownish-yellow needles from alcohol (N found, 19·3; theo., 19·7%).

(4) Azo-indamine dye: *Indamine-3-azodimethylaniline* (IV), from diazotised phenylene-blue; violet, microscopic needles from chloroform (N found, 21·5; theo., 21·3%).

(5) Azo-indigoid dyes: (*a*) *Indigotin-5-azodimethylaniline* (V*a*), from diazotised 5-aminoindigotin; violet needles with silky lustre from pyridine (N found, 17·3; theo., 17·1%). (*b*) *Indigotin-4 : 4′-bisazodimethylaniline* (V*b*), from tetrazotised 4 : 4′-diaminoindigotin (*Monatsh.*, 1905, **62**, 1262); brownish-yellow, microscopic needles from acetic acid (N found, 19·3; theo., 19·2%).

(6) Azo-thioindigoid dye: "*Thioindigo*"-5 : 5′-*bisazodimethylaniline* (VI), from tetrazotised 5 : 5′-diaminothioindigo (D.R.-P. 240805); light brown, amorphous powder (N found, 14·5; theo., 14·2%).

Series V. Reduplication of the Same Chromophore.

A. *The Azo-group.*—1. *Benzeneazobenzeneazobenzeneazophenol*, $Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$. Benzeneazobenzeneazoaniline (*Ber.*, 1888, **21**, 2145) (1 mol.) was diazotised in cold concentrated hydrochloric acid solution, and the product coupled with phenol (1 mol.), dissolved in excess of sodium hydroxide, in the usual manner. The final product crystallised from glacial acetic acid in bright yellow prisms, m. p. 248° (Found: N, 20·4. $C_{24}H_{18}ON_6$ requires N, 20·7%).

2. *Benzeneazobenzeneazobenzeneazoaniline*,

$$Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2,$$

was obtained by coupling diazotised benzeneazobenzeneazoaniline (1 mol.) with aniline (1 mol.) dissolved in the minimum quantity of strong hydrochloric acid and, after thorough stirring, adding an excess of sodium acetate. The product crystallised from alcohol in yellow leaflets, m. p. 194°. No diazoamino-compound was formed (Found: N, 24·4. $C_{24}H_{19}N_7$ requires N, 24·2%).

3. *Benzeneazobenzeneazobenzeneazodimethylaniline*,

$$Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NMe_2,$$

was prepared in a similar way to the above by using dimethylaniline in place of aniline. It crystallised from alcohol in orange leaflets, m. p. 218° (Found: N, 22·8. $C_{26}H_{23}N_7$ requires N, 22·6%).

4. *Benzeneazobenzeneazobenzeneazobenzeneazophenol*,

$$Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH,$$

was obtained by diazotising benzeneazobenzeneazobenzeneazoaniline (1 mol.) in cold strong sulphuric acid solution and coupling the product with phenol (1 mol.), dissolved in excess of sodium hydroxide, in the usual way. It crystallised from nitrobenzene in brownish-yellow prisms, not melting at 290° (Found: N, 22·3. $C_{30}H_{22}ON_8$ requires N, 22·9%).

5. *Benzeneazobenzeneazobenzeneazobenzeneazodimethylaniline*,

$$Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NMe_2,$$

was prepared by adding diazotised benzeneazobenzeneazobenzeneazoaniline (1 mol.) to dimethylaniline (1 mol.), dissolved in concentrated hydrochloric acid, and, after thorough stirring, adding an excess of sodium acetate. It crystallised from pyridine in orange-yellow prisms, not melting at 290° (Found: N, 23·2. $C_{32}H_{27}N_9$ requires N, 23·4%).

B. *The Diphenylmethane Group.*—1. *Bistetramethyldiaminodiphenylmethane*, $(NMe_2{\cdot}C_6H_4)_2CH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$. A mixture of 10 g. of glyoxal, 22 g. of dimethylaniline, and 50 c.c. of fuming hydrochloric acid was heated in a sealed tube at 180° for 8 hours. The product was diluted with water, rendered alkaline with sodium carbonate, and distilled in steam until no more dimethylaniline passed over. The residue, which solidified on cooling, was ground up, washed with water, and its solution in dilute hydrochloric acid was decolorised by boiling with animal charcoal and sulphurous acid. The filtered solution on treatment with dilute sodium hydroxide gave a white precipitate of the leuco-base, which was filtered off, washed, and dried on a porous plate; it crystallised from ether in colourless needles, m. p. 96—98°, which became brownish-violet on exposure to air (Found: N, 11·4. $C_{34}H_{42}N_4$ requires N, 11·1%).

2. *Bistetramethyldiaminodiphenylcarbinol* (*diacetate*),

$$\begin{matrix} C_2H_3O_2{\cdot}Me_2N{:}C_6H_4 \\ Me_2N{\cdot}C_6H_4 \end{matrix}\!\!>\!C\!-\!C\!<\!\begin{matrix} C_6H_4{\cdot}{:}NMe_2{\cdot}C_2H_3O_2 \\ C_6H_4{\cdot}NMe_2 \end{matrix}$$

The above leuco-base was dissolved in sufficient 50% acetic acid, slightly more than the calculated quantity of freshly precipitated manganese dioxide added, and the mixture thoroughly stirred. The solution, dark green at first, on warming on the steam-bath became brilliant violet-blue. After heating for about an hour, it was filtered, cooled, and treated with an excess of saturated sodium acetate solution. The precipitated colouring matter was filtered off, washed, and dried; it crystallised from chloroform–ligroin in dark violet-blue needles with a coppery lustre which dissolved in organic solvents and dilute acids with a violet-blue colour (Found: N, 9·3. $C_{38}H_{46}O_4N_4$ requires N, 9·0%).

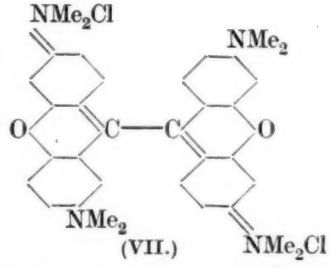
C. *The Triphenylmethane Group.*—1. leuco-*Dimalachite-green*, $(NMe_2\cdot C_6H_4)_2CH\cdot C_6H_4\cdot C_6H_4\cdot CH(C_6H_4\cdot NMe_2)_2$. *p*-Bromo*leuco*malachite-green [m. p. 128°, obtained from *p*-bromobenzaldehyde (1 mol.) and dimethylaniline (2 mols.), concentrated hydrochloric acid at 200° being used as the condensing agent] was intimately mixed with an equal weight of very fine copper bronze, and the mixture heated at 210—220° in an atmosphere of hydrogen. In 1 hour, a reaction took place which was indicated by the loss of metallic lustre of the bronze powder. After heating for about 4 hours, the melt was dissolved in dilute hydrochloric acid, the solution filtered, the filtrate decolorised with animal charcoal and sulphur dioxide, and the leuco-base precipitated with dilute sodium hydroxide. It could not be crystallised and was a white powder, m. p. 135—138°, which readily became green on exposure to air (Found: N, 8·2. $C_{46}H_{50}N_4$ requires N, 8·5%).

2. *Dimalachite-green* (*diacetate*),

$$\begin{matrix} OAc\cdot NMe_2 & & & & C_6H_4\cdot NMe_2\cdot OAc \\ : & C_6H_4 & \rangle & C\cdot C_6H_4\cdot C_6H_4\cdot C & \langle & : \\ NMe_2\cdot C_6H_4 & & & & C_6H_4\cdot NMe_2 \end{matrix},$$

prepared by oxidising the above leuco-base with manganese dioxide, could not be crystallised and was obtained as a brilliant green powder which dissolved in organic solvents and dilute acids with a deep green colour (Found: N, 7·6. $C_{50}H_{54}O_4N_4$ requires N, 7·2%).

D. *The Pyronine Group.—Dipyronine* G (formula VII). Glyoxal (1 mol.), dimethyl-*m*-aminophenol (4 mols.), and strong hydrochloric acid (10 mols.) were heated together on the steam-bath for about 12 hours under reflux in a current of carbon dioxide. The product was diluted with water, and the leuco-base precipitated with sodium carbonate. As it could not be purified in this state, being very easily oxidised in the air, it was repeatedly dissolved in dilute hydrochloric acid and reprecipitated with sodium carbonate before being converted into the dye. This conversion was done by dissolving the leuco-base in cold strong sulphuric acid and adding



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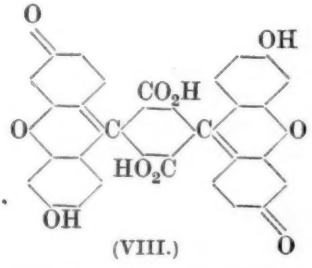


(VIII.)

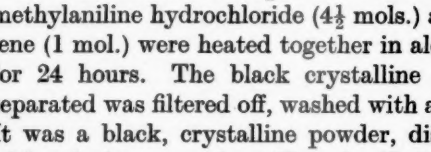
slightly more than the calculated quantity of sodium nitrite, with vigorous stirring. The solution became dark red and small steel-

blue needles began to separate. After 1 hour, the solution was poured into ice-water, and the dye precipitated by adding a concentrated solution of sodium chloride. It came down in fine steel-blue needles with a golden iridescence, and was filtered off, washed with a little water, and dried. Its solutions in water and in organic solvents have a brilliant pink colour (Found: N, 9·6. $C_{34}H_{36}O_2N_4Cl_2$ requires N, 9·3%).

E. *The Phthalein Group.—Difluorescein* (VIII) was obtained by condensing pyromellitic acid with resorcinol (4 mols.) according to the method (J., 1906, **89**, 1787) by which the corresponding compound was prepared from mellitic acid. It is a dark yellow, amorphous substance, not melting at 300° (Found: C, 69·5; H, 3·4. $C_{34}H_{18}O_{10}$ requires C, 69·6; H, 3·0%).

F. *The Oxazine Group.—Di-Meldola's blue* (IX). *p*-Nitrosodimethylaniline hydrochloride (4½ mols.) and 2 : 7-dihydroxynaphthalene (1 mol.) were heated together in alcoholic solution under reflux for 24 hours. The black crystalline colouring matter that had separated was filtered off, washed with alcohol and water, and dried. It was a black, crystalline powder, dissolving in organic solvents with a dark green colour (Found: N, 11·6. $C_{26}H_{22}O_2N_4Cl_2$ requires N, 11·3%).

(IX.)



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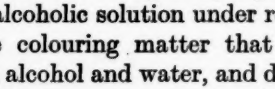
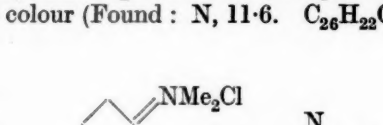


(XI.)



G. *The Azine Group.*—1. *Phenazineazine* (X) was obtained by condensing 2 : 3-diaminophenazine (*Ber.*, 1889, **22**, 356) with *o*-benzoquinone in concentrated sulphuric acid solution. It crystallises from nitrobenzene, and also sublimes on careful heating, in bright yellow needles which do not melt at 290° (Found: N, 19·7. $C_{18}H_{10}N_4$ requires N, 19·8%).

2. *Phenazineazineazine* (XI) was obtained by condensing 2 : 3-diaminophenazine with 2 : 3-dihydroxyphenazine (*Ber.*, *loc. cit.*) in cold strong sulphuric acid solution containing 30% of sulphur trioxide. It crystallises from nitrobenzene in microscopic yellow

needles which do not melt at 290° (Found: N, 21·6. $C_{24}H_{12}N_6$ requires N, 21·8%).

Series VI.

A. *Malachite-green with a Bridge Linking between Two Benzene Nuclei.*—1. 3 : 3′-*Tetramethyldiaminodiphenyl*,

$$NMe_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NMe_2.$$

3 : 3′-Dinitrodiphenyl (*Ber.*, 1901, **34**, 2177) was reduced with tin and hydrochloric acid in the usual way, the tin precipitated with hydrogen sulphide, and the filtered solution evaporated to dryness. The hydrochloride of 3 : 3′-diaminodiphenyl, thus obtained in long, colourless, silky needles, was dissolved (10 g.) in 150 c.c. of water, and 60 g. of methyl sulphate were added, about 5 g. at a time with vigorous shaking, during an hour, the solution being neutralised from time to time with 10% sodium hydroxide solution; methylation was complete when excess of sodium hydroxide failed to precipitate any amino-compound. The yellow crystalline chromate of the quaternary base precipitated from this solution by a strong aqueous solution of chromic acid was filtered off, washed with water, and treated in aqueous suspension with sulphur dioxide. The dark green solution thus obtained was boiled to drive off the excess of sulphur dioxide and rendered strongly alkaline with ammonia, the precipitated chromium hydroxide washed with water, and the filtrate and washings were evaporated to dryness. The residue was extracted with absolute alcohol, and the extract, after being distilled on the steam-bath until no more alcohol came over, was heated at 250° in a vacuum for ½ hour; only a small, pale yellow distillate, however, was obtained. The distillate and the residue were dissolved in hot dilute hydrochloric acid and the solution was decolorised with animal charcoal. From the filtered solution dilute aqueous sodium hydroxide precipitated a solid, which crystallised from alcohol in clusters of colourless needles, m. p. 126—128°, easily soluble in dilute mineral acids (Found: N, 11·5. $C_{16}H_{20}N_2$ requires N, 11·8%).

2. *The leuco-base*, 3 : 6-*tetramethyldiamino*-9-*phenylfluorene* (XII). A solution of 3 : 3′-tetramethyldiaminodiphenyl (1 mol.) and benzal chloride (1 mol.) in dry carbon disulphide was heated under reflux with powdered anhydrous aluminium chloride (2 mols. plus 10% excess) for about 6 hours. The carbon disulphide was distilled off, the dark brown aluminium compound decomposed with water, and the white residue filtered, washed, and extracted with very dilute acetic acid (in which 3 : 3′-tetramethyldiaminodiphenyl is insoluble). The extract was rendered alkaline with sodium carbonate, and the precipitated leuco-base filtered off and washed with

TABLE II.

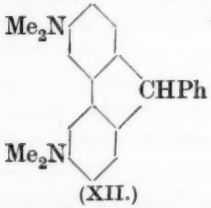
Absorption Maxima of Azotriphenylmethane Dyes.

The dye whose symbolical formula is in the first column was prepared from the aldehyde, the reference number of which is in the second column. *a* denotes the absorption maximum of the dye in alcoholic solution containing 1 mol. of HCl, and in the last column are its found and theoretical (in brackets) percentages of nitrogen. A = $C_6H_5{\cdot}N{:}N{\cdot}$ or $\cdot C_6H_4{\cdot}N{:}N{\cdot}$, B = C_6H_5 or C_6H_4, etc., C = methane carbon atom, and R and R′ respectively = and .

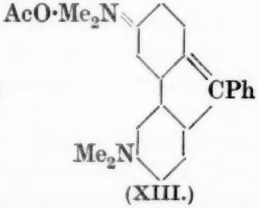
Formula.	Aldehyde.	*a*.	N %.
B·C:RR′ (malachite-green).	—	6190	—
A·B (azobenzene).	—	4310	—
A·R (butter-yellow).	—	5040	—
A·B·C:RR′.	I, 1	5720	11·5 (11·2)
(4)HO·B·A·C:RR′.	I, 2	5560	11·3 (11·0)
(4)HO·B·C:RR′.	—	5960	(J., 1917, **111**, 815)
(4)HO·B·A·A·C:RR′.	I, 13	5580	14·1 (13·7)
(2 : 4)$(HO)_2$B·C:RR′.	—	6010	(J., *ibid.*)
(2 : 4)$(HO)_2$B·A·C:RR′.	I, 11	5650	11·0 (10·7)
(2 : 3 : 4)$(HO)_3$B·C:RR′.	—	6120	(J., *ibid.*)
(2 : 3 : 4)$(HO)_3$B·A·C:RR′.	I, 12	5670	10·8 (10·4)
R·C:RR′ (crystal-violet).	—	5990	—
R·A·C:RR′.	I, 3	5570	13·4 (13·0)
R·A·A·C:RR′.	I, 14	5580	15·8 (15·3)
(3)HO·B·C:RR′ (patent blue).	—	6010	7·1 (6·9)
(4)HO·B·(1)A·(3)C:RR′.	I, 5	5650	11·8 (11·0)
(4)HO·B·A·(1)A·(3)C:RR′.	I, 15	5780	14·0 (13·7)
(2)HO·B·(1)C:RR′.	—	5990	7·2 (6·9)
A(4), HO(2)>B·(1)C:RR′.	I, 8	5570	11·9 (11·8)
(4)MeO·B·C:RR′.	—	6050	(*Ber.*, 1881, **14**, 2523)
(4)MeO·B·A·C:RR′.	I, 10	5610	10·9 (10·7)
(1)HO·A(4), HO(2)>B·(1)C:RR′.	I, 9	5650	11·1 (10·7)

water. It could not be crystallised and melted at 92—94° (Found: N, 8·7. $C_{23}H_{24}N_2$ requires N, 8·5%).

3. *The dye* (*acetate*) (XIII). The above leuco-base was oxidised in 50% acetic acid solution with freshly precipitated manganese dioxide in the usual manner. It was obtained from chloroform–ligroin as a dark green, crystalline powder, which formed dark green solutions in organic solvents and dilute acids (Found: N, 7·5. $C_{25}H_{26}O_2N_2$ requires N, 7·2%).



(XII.)



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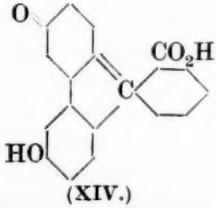


(XIV.)

B. *Phenolphthalein with a Bridge across two Benzene Nuclei* (XIV). —A mixture of 9 g. of 3 : 3′-dihydroxydiphenyl (*Ber.*, 1894, **27**,

2107), 7·5 g. of phthalic anhydride, and 15 g. of anhydrous aluminium chloride was heated at 200° for 5 hours. The product was powdered, extracted with boiling water, the residue dissolved in hot aqueous sodium carbonate, the solution filtered, and the filtrate acidified; the dye was thus obtained in pale purple flocks. It crystallised from glacial acetic acid (animal charcoal) in colourless needles, not melting at 285°. It dissolved in alkalis with a bluish-red colour (Found: C, 75·7; H, 4·0. $C_{20}H_{12}O_4$ requires C, 75·9; H, 3·7%).

Table III.

Absorption Maxima of Azotriphenylmethane Dyes (Series II and III).

These dyes were prepared by tetrazotising the amines referred to in the second column, coupling the products with dimethylaniline (2 mols.), and oxidising the final products. *a* is now the absorption maximum of the dye in conc. HCl.

Formula.	Amine.	*a*.	N %.
B·C(OH):$(A·R)_2$.	II, 1	5050	15·5 (15·1)
(4)OH·B·C(OH):$(A·R)_2$.	II, 2	5140	15·1 (14·7)
R·C(OH):$(A·R)_2$.	II, 3	5160	16·1 (16·4)
B·A·CH:$(A·R)_2$.	III, 1	5070	17·8 (17·4)
(4)OH·B·A·CH:$(A·R)_2$.	III, 3	5070	17·5 (17·0)
R·A·CH:$(A·R)_2$.	III, 2	5070	18·2 (18·3)

Table IV.

Absorption Maxima of Azo-dyes of the Mixed Type (Series IV).

Name or reference.	Absorption maxima (λ).	Name or reference.	Absorption maxima (λ).
Nile-blue A	6040	Indigotin	6050
IV, 1	5820	5-Aminoindigotin	5890
Lauth's-violet	5970	IV, 5*a*	5720
IV, 2	5050	4 : 4′-Diaminoindigotin	5940
Phenylene-blue	6600	IV, 5*b*	5010
IV, 4	5980	"Thioindigo"	5240
Phenosafranine	5250	5 : 5′-Diaminothioindigo	5230, 5920
IV, 3*a*	5790	IV, 6	4990
IV, 3*b*	5130		

Absorption Maxima of Dyes with Reduplicated Chromophores (Series V).

Benzeneazophenol	4330	Malachite-green	6190
Benzeneazobenzeneazophenol	4350	V, C 2	6220
V, A 1	4360	Pyronine	5380 (6670)
V, A 4	4360	V, D	5380 (6680)
Benzeneazodimethylaniline	5040	Meldola's blue	6060
Benzeneazobenzeneazodimethylaniline	5090	V, F.	7020
V, A 3	5130	Phenazine	4290
V, A 5	5140	V, G 1	4310
Michler's hydrol	6080	V, G 2	4320
V, B 2	5990	Fluorescein	4940
		V, E	4950
		VI, A 3	6210
		Phenolphthalein	5540
		VI, B	5550

My best thanks are due to Professor J. F. Thorpe, F.R.S., for the kind interest he has taken in this work, to Professor A. Fowler, F.R.S., for permission to use his quartz spectrograph, and to the Chemical Society for a grant which has defrayed part of the expense of this research.

IMPERIAL COLLEGE, SOUTH KENSINGTON. [*Received, October 30th*, 1925.]

CLI.—*Studies on the Walden Inversion. Part X. The Reaction between Water and the Phenylchloroacetate and Phenylbromoacetate Ions.*

By ALLAN MILES WARD.

RACEMISATION may be effected by two processes apparently distinct, namely (1) without displacement of groupings, and (2) during group-displacement. Catalytic racemisation falls under case (1). The generally accepted mechanism of (1) is that the racemisation is due either (*a*) to a tautomeric change, or (*b*) to an equilibrium existing between the original substance and the products formed by its dissociation, one of which is unsaturated at the asymmetric centre (compare Lowry, *Rep. Brit. Assoc.*, 1904; McKenzie and Widdows, J., 1915, **107**, 702; McKenzie and Wren, J., 1919, **115**, 602; Walden, "Optische Umkehrerscheinungen," 1919, V Kapitel). By such a mechanism the resulting mixture of optical isomerides, if not quite inactive, must contain an excess of the isomeride initially present, a Walden inversion thus being impossible. This statement, however, would not be applicable in the case of asymmetric catalytic racemisation (McKenzie and Smith, *Ber.*, 1925, **58**, 894). On the other hand, racemisation of type (2) may be effected by the occurrence of two simultaneous reactions, whereby both *d*- and *l*-isomerides of the product are formed as follows:

$$d\text{B} \xleftarrow{k_1} d\text{A} \xrightarrow{k_2} l\text{B}.$$

The two reactions, which may be identical from the ordinary kinetic standpoint, proceed with velocities, the coefficients of which, k_1 and k_2, may be equal or different. The relative values of k_1 and k_2 might vary largely according to the experimental conditions, so that in some cases k_2 would be negligible in comparison with k_1, when only one isomeride would result. When k_1 and k_2 become equal, the product would be entirely racemic; whilst, depending on the relative values of k_1 and k_2, a complete range of intermediate activities of either sign is possible. By such a mechanism a Walden inversion may thus be effected. This view has been suggested in

various forms many times previously (compare Fischer, *Annalen*, 1911, **381**, 126; Werner, *ibid.*, 1912, **386**, 68), and the experiments of Holmberg, whereby active products of either sign are produced from a given initial material, provide a proof for the case in which the mechanisms of the production of the two isomerides differ when deduced from the ordinary kinetic standpoint. Thus the kinetic results (Holmberg, *J. pr. Chem.*, 1913, **87**, 456) show that the conversion of sodium or silver *l*-bromosuccinate into malic acid proceeds through an intermediate stage, since definitely established as malolactone. If this reaction is carried out in acid solution, the product from *l*-bromosuccinic acid is *r*- and *l*-malic acids, whilst in alkaline solution *r*- and *d*-malic acids are formed. Holmberg represented this by the following scheme :

l-Bromosuccinic acid as sodium salt

↓

d-rotatory bromine-free intermediate compound

(in acid solution) | | (in alkaline solution)

↓ ↓

l-malic acid *d*-malic acid.

This scheme closely resembles the one used above, but the mechanism of the production of the malic acids from the lactone is not discussed, and appears to be more allied to Phillips's investigations (J., 1923, **123**, 22; Kenyon, Phillips, and Turley, J., 1925, **127**, 399; Phillips, *ibid.*, p. 2563) than to the present work, the reaction probably taking place by the fission of one or other of the bonds in malolactone as indicated in positions (*a*) and (*b*)

$$\underset{\underset{(a)}{\vdots}\quad\underset{(b)}{\vdots}}{\mathrm{CO{\cdot}CH_2{\cdot}CH{\cdot}CO_2'}}$$
$$\mathrm{O}$$

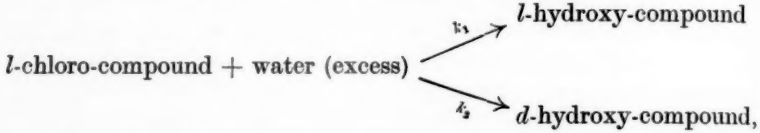
In the subsequent experiments on the xanthosuccinic acids and the thiolmalic acids (Holmberg, *J. pr. Chem.*, 1913, **88**, 553; *Arkiv Kemi, Min., Geol.*, 1916, **6**, No. 1; 1916, **6**, No. 8; Holmberg and Lenander, *ibid.*, 1917, **6**, No. 17) evidence from kinetic results shows the reaction to proceed both by direct substitution of the halogen and also *via* the lactone, and from experiments with the reactants in various concentrations, the following mechanism was put forward for the conversion into the thiolmalic acids (and similarly for the xanthosuccinic acids) :

(*a*) $l\text{-MO}_2\text{C{\cdot}CH}_2\text{{\cdot}CHBr{\cdot}CO}_2\text{M} + \text{MS}\dot{\text{H}} \longrightarrow d\text{-MO}_2\text{C{\cdot}CH}_2\text{{\cdot}CH(SH){\cdot}CO}_2\text{M} + \text{MBr}.$

(*b*) $l\text{-MO}_2\text{C{\cdot}CH}_2\text{{\cdot}CHBr{\cdot}CO}_2\text{M} \longrightarrow d\text{-CO{\cdot}CH}_2\text{{\cdot}CH{\cdot}CO}_2\text{M} \longrightarrow l\text{-MO}_2\text{C{\cdot}CH}_2\text{{\cdot}CH(SH){\cdot}CO}_2\text{M}.$

The mechanisms for the production of the stereoisomeric thiolmalic acids (and xanthosuccinic acids) are here kinetically different, whereas in the present investigation the mechanisms are the same from the ordinary kinetic point of view.

Considered on a quantitative basis, the reaction (*e.g.*)



in order to fulfil the conditions of the above mechanism, must (from the results of kinetic measurements) be one of a simple order, and the value of k thus calculated will be equal to $k_1 + k_2$, whilst, from the results of measurements of the change of rotation of the solution of the active substance with time under the same conditions as employed for the inactive, the same value of k should result. To test these considerations the conversion of sodium *l*-phenylchloroacetate into sodium *r*- and *l*-mandelate has been carried out. The action of water on *l*-phenylchloroacetic acid, of water on sodium *l*-phenylchloroacetate, and of aqueous sodium hydroxide on sodium *l*-phenylchloroacetate was first studied by McKenzie and Clough (J., 1908, **93**, 811; 1909, **95**, 777), who found that the mandelic acid produced was lævorotatory and that extensive racemisation occurred in these changes. The kinetics of the conversion of *r*-phenylchloroacetic acid and its sodium salt in aqueous solution, and also of the sodium salt in aqueous caustic soda solution, have been investigated (Senter, J., 1915, **107**, 908), and it was shown that each of the above reactions is one and the same, namely, the reaction of water with the phenylchloroacetate ion. The best value for the velocity coefficient for the conversion of sodium *r*-phenylchloroacetate in aqueous sodium hydroxide solution at 25° was considered to be 0·00146, where time is measured in minutes, but the values of k actually found (*loc. cit.*, p. 914) at 25° for the sodium salt ($N/10$) were

(*a*) in caustic soda ($N/10$), 0·00138, 0·00142, 0·00145,
(*b*) ,, ,, ($N/5$), 0·00134, 0·00134, 0·00138.

Thus the reaction here dealt with is $PhCHCl{\cdot}CO_2' + H_2O(\text{excess}) \longrightarrow PhCH(OH){\cdot}CO_2' + NaCl$ from the kinetic point of view. Table I gives the results of the corresponding polarimetric experiment, which was carried out as follows. To 150 c.c. of aqueous sodium hydroxide (0·1858N) at 24·85° were added 2·3037 g. of *l*-phenylchloroacetic acid with $[\alpha]^{16°}_{5780}$ — 191·5° in benzene (resolved by the method of McKenzie and Clough, *loc. cit.*, except that the morphine salt was

decomposed by dilute aqueous ammonia). The acid rapidly dissolved to a clear, colourless solution, which was maintained at 24·85°. Samples were withdrawn at the times shown in Table I, and their rotations determined, using a 2-dcm. tube and the yellow mercury line.

TABLE I.

			k.	
Time.	θ_t (obs.).	θ_t (calc.).	Differential.	Integral.
0 mins.	−[4·52]			
7	4·50			
39	4·24	−4·25	0·0019	0·00168
61	4·12	4·11	0·0013	0·00156
121	3·75	3·74	0·0016	0·00158
181	3·38	3·33	0·0018	0·00165
240	3·05	3·10	0·0018	0·00169
300	2·82	2·83	0·0014	0·00162
360	2·55	2·58	0·0018	0·00164
420	2·35	2·35	0·0014	0·00161
480	2·15	2·14	0·0016	0·00160
543	2·00	1·95	0·0012	0·00156
600	1·76	1·79	0·0024	0·00164
665	1·59	1·62	0·0017	0·00164
730	1·50	1·47	0·0010	0·00158
1510	0·54	0·50	0·0013	0·00154
1773	0·38	0·36	0·0017	0·00157
2037	0·26	0·28	0·0022	0·00166
2931	0·16	0·15	0·0011	0·00153
5 days	0·11			
8	0·10			
17	0·11		Mean 0·0016	Mean 0·00161

The values of k differential (column 4) are obtained from the formula

$$k = \frac{\delta\theta}{\delta t} \cdot \frac{2}{\theta_{t_2} + \theta_{t_1} - 2\theta_\infty}$$

where θ_{t_2} and θ_{t_1} are consecutive observations, $\delta\theta = \theta_{t_2} - \theta_{t_1}$ and $\delta t = t_2 - t_1$. The values of k thus calculated are irregular, as is only to be expected, since a small error in the determination of θ_t causes, by this method, a large variation in the coefficient. No drift in value, however, occurs, and the applicability to this case is thus shown of the integrated form (column 5) for a unimolecular reaction, namely, $k = \frac{2{\cdot}3}{t} \log_{10} \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}$.

This method of calculation does, however, suffer from the defect that great importance is placed on the value of θ_0, but the mean value of k obtained by both methods is substantially the same. A duplicate determination using an acid with $[\alpha]_{5780} - 188°$ gave $k = 0{\cdot}00160$.

It would thus appear that the mechanism is in the main as postulated, but the divergence between the values of the coefficients

as thus calculated and those of Senter (*loc. cit.*) remains to be accounted for. The following experiment on sodium *l*-mandelate showed that under the conditions of the preceding experiments mandelic acid does not undergo catalytic racemisation, at least with any speed comparable with that of the displacement here studied. To 1·3865 g. of *l*-mandelic acid with $[\alpha]^{15°}_{5780}$ — 159° in water, was added a mixture of 50 c.c. of sodium chloride (0·2020*N*) and 50 c.c. of aqueous sodium hydroxide (0·1858*N*) at 24·85°. The solution was maintained at this temperature, and samples were withdrawn at intervals and their rotations determined, the yellow mercury line and a 2-dcm. tube being used. The results are shown below :

Time (hours)	0·10	2·05	12·05	30·5	50·0	3 days	9 days
Rotation ...	−3·25°	−3·43°	−3·35°	−3·43°	−3·44°	−3·44°	−3·44°.

Thus no contributory factor here arises to produce the difference in the two values. There remains the slight possibility that the coefficient for sodium *l*-phenylchloroacetate is not the same as that for sodium *r*-phenylchloroacetate, but this was disposed of by carrying out experiments (*a*) and (*b*) below.

(*a*) To 1·4822 g. of *l*-phenylchloroacetic acid, with $[\alpha]^{24°}_{5780}$ — 188° at 24·85°, were added 100 c.c. of sodium hydroxide (0·2010*N*). Samples of 10 c.c. were withdrawn at times shown, and titrated against sulphuric acid (1·037 × *N*/20), phenolphthalein being used as indicator.

(*b*) This experiment was carried out simultaneously with (*a*), and the conditions were identical, except that 1·5816 g. of *r*-phenylchloroacetic acid were used.

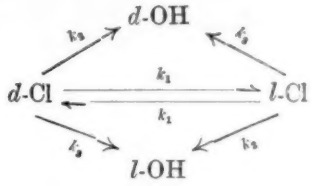
The results are in Table II, k being equal to $2{\cdot}3/t \,.\, \log_{10} a/(a - x)$.

TABLE II.

l-Acid.			*r*-Acid.		
Time.	Titre.	k.	Time.	Titre.	k.
3 mins.	21·45		4 mins.	20·43	
60	20·38		60	19·13	
179	18·22	0·00128	180	16·84	0·00126
360	15·42	0·00131	360	13·89	0·00129
540	13·31	0·00129	540	11·57	0·00130
660	12·03	0·00131	660	10·20	0·00133
1500	7·41	0·00131	1500	5·10	0·00138
4 days	5·09		6 days	2·87	
	Mean	0·00130		Mean	0·00131

It thus appears certain there is a divergence between the values of k as determined from titres and from optical measurements, and this may be satisfactorily accounted for by assuming that, in addition to the displacement racemisation of the phenylchloro-

acetate ion, there is a simultaneous catalytic racemisation of this ion, so that the completed scheme would become :



If a is the initial concentration of d-chloro-compound, b the initial concentration of l-chloro-compound, x and y the amounts of d- and l-chloro-compounds respectively changed in time t,

then $dx/dt = k_1(a - x) - k_1(b - y) + (k_2 + k_3)(a - x)$. (1)

and $dy/dt = k_1(b - y) - k_1(a - x) + (k_2 + k_3)(b - y)$. (2)

Integration of (1) and (2) gives

$$x = a - \frac{a + b}{2}e^{-(k_2 + k_3)t} - \frac{a - b}{2}e^{-(2k_1 + k_2 + k_3)t} \quad . \quad (3)$$

and $$y = b - \frac{a + b}{2}e^{-(k_2 + k_3)t} + \frac{a - b}{2}e^{-(2k_1 + k_2 + k_3)t} \quad . \quad (4)$$

For the hydroxy-compounds, if w_d and w_l are the concentrations of d- and l- forms, respectively, present at time t,

then $$dw_d/dt = k_2(a - x) + k_3(b - y) \quad . \quad (5)$$

Substituting in (5) the values of x and y in (3) and (4) and integrating

$$w_d = -\frac{a + b}{2}e^{-(k_2 + k_3)t} - \frac{k_2 - k_3}{2k_1 + k_2 + k_3} \cdot \frac{a - b}{2} \cdot e^{-(2k_1 + k_2 + k_3)t} + \frac{(k_1 + k_2)a + (k_1 + k_3)b}{2k_1 + k_2 + k_3}.$$

Similarly

$$w_l = -\frac{a + b}{2}e^{-(k_2 + k_3)t} - \frac{k_3 - k_2}{2k_1 + k_2 + k_3} \cdot \frac{a - b}{2} \cdot e^{-(2k_1 + k_2 + k_3)t} + \frac{(k_1 + k_3)a + (k_1 + k_2)b}{2k_1 + k_2 + k_3}.$$

Thus at any time t, the observed rotation of the solution (θ_t) is equal to the rotation of the chloro-compounds + the rotation of the hydroxy-compounds, *i.e.*, $\theta_t = D_{Cl}\{(a - x) - (b - y)\} + D_{OH}(w_d - w_l)$, where D_{Cl}, D_{OH} are the rotations of unit concentrations

of *d*-chloro- and *d*-hydroxy-compounds, respectively, under the given conditions, *i.e.*,

$$\theta_t = D_{Cl}\{(a-b)e^{-(2k_1+k_2+k_3)t}\} + D_{OH}\cdot\frac{(k_2-k_3)(a-b)}{2k_1+k_2+k_3}\{1-e^{-(2k_1+k_2+k_3)t}\}.$$

In the present case, $a = 0$, so that

$$\theta_t = -D_{Cl}\cdot b\cdot e^{-(2k_1+k_2+k_3)t} - D_{OH}\cdot b\cdot\frac{k_2-k_3}{2k_1+k_2+k_3}\{1-e^{-(2k_1+k_2+k_3)t}\} \quad (6)$$

To evaluate k_1, k_2 and k_3, we have from (6) when $t = 0$,

$$\theta_0 = -D_{Cl}\cdot b = -4{\cdot}52 \text{ (Table I)} \quad . \quad . \quad . \quad (7)$$

and when $t = \infty$,

$$\theta_\infty = -D_{OH}\cdot b\cdot\frac{k_2-k_3}{2k_1+k_2+k_3} = -0{\cdot}11 \text{ (Table I)}.$$

Substituting in (6),

$$\theta_t = -4{\cdot}52e^{-(2k_1+k_2+k_3)t} - 0{\cdot}11 + 0{\cdot}11e^{-(2k_1+k_2+k_3)t}$$
$$= -4{\cdot}41e^{-(2k_1+k_2+k_3)t} - 0{\cdot}11,$$

i.e.,
$$e^{(2k_1+k_2+k_3)t} = \frac{-4{\cdot}41}{\theta_t+0{\cdot}11} = \frac{\theta_0-\theta_\infty}{\theta_t-\theta_\infty},$$

therefore $2k_1 + k_2 + k_3 = \frac{2{\cdot}3}{t}\log_{10}\frac{\theta_0-\theta_\infty}{\theta_t-\theta_\infty} = 0{\cdot}00161$ (Table I)

and $k_2 + k_3 = 0{\cdot}00130$ (Table II), so that $k_1 = 0{\cdot}000155$.

Further, from the data on p. 1188, 2·054 g. of mandelic acid (= 2·3037 g. of phenylchloroacetic acid) have rotation $-3{\cdot}39° = -D_{OH}\cdot b$.

Therefore from (7), $-0{\cdot}11 = -3{\cdot}39\frac{k_2-k_3}{0{\cdot}00161}$, so that $k_2 - k_3 = 0{\cdot}000052$, whence $k_2 = 0{\cdot}000676$ and $k_3 = 0{\cdot}000624$ and $\theta_t = -4{\cdot}41e^{-0{\cdot}00161t} - 0{\cdot}11$.

For comparison with the observed values of θ_t, those values thus calculated are shown in column 3, Table I.

The divergence between the coefficients from the corresponding titration and optical experiments is thus satisfactorily accounted for by assuming that besides the displacement racemisation, there is also a catalytic racemisation.

It becomes of interest to review in the same way the results of McKenzie and Walker (J., 1915, **105**, 1685) on the conversion of *l*-phenylbromoacetic acid and its sodium salt in aqueous and aqueous caustic soda solutions, in conjunction with the corresponding kinetic experiments of Senter and Tucker (J., 1916, **107**, 690). The experiments of Senter and Tucker on the reactions between water and *r*-phenylbromoacetic acid and its sodium salt, and also

between aqueous caustic soda and sodium *r*-phenylbromoacetate, showed that the main reaction in each case consists of the interaction of water and the phenylbromoacetate ion, exactly as for phenylchloroacetic acid. From the results on the bromo-acid, it was considered that in this case water also reacts with the undissociated acid, the reaction between water and the ion being some 120 times faster than between water and the undissociated acid. The main reaction here dealt with is, therefore, $PhCHBr{\cdot}CO_2' + H_2O(\text{excess}) \longrightarrow PhCH(OH){\cdot}CO_2'$. As for the chloro-acid, the rate of reaction is thus dependent on the hydrogen-ion concentration, and development of hydrogen ions during the reaction causes a marked falling off in the value of the velocity coefficient. McKenzie and Walker found in some of their experiments that the reaction between water and *l*-phenylbromoacetic acid gave *d*- and *r*-mandelic acids, whilst in other cases *l*- and *r*-acids resulted, and to account for this the following scheme was put forward (*loc. cit.*, p. 1689):

(I) *l*-$PhCHBr{\cdot}CO_2H + H_2O = HBr +$ *r*- and *l*-$PhCH(OH){\cdot}CO_2H$

(II) *r*- and *l*-$PhCH(OH){\cdot}CO_2H + HBr = H_2O +$ *r*- and *d*-$PhCHBr{\cdot}CO_2H$

(III) *r*- and *d*-$PhCHBr{\cdot}CO_2H + H_2O = HBr +$ *r*- and *d*-$PhCH(OH){\cdot}CO_2H$.

The changes of rotation involved in the cases on which this theory is based were very small. Thus from the data in Table I (*loc. cit.*, p. 1693) the change is from $-0{\cdot}02°$ to $+0{\cdot}04°$. Assuming that the *l*-rotation due to the mandelic acid when (I) is complete is $-0{\cdot}02°$, if no racemisation at all took place in (II) and (III), then the rotation of the *d*-mandelic acid would be $+0{\cdot}02°$, and could not be $+0{\cdot}04°$ by this mechanism, although a difference of $\pm 0{\cdot}02°$ is within the limits of experimental error. If, however, it is assumed that (II) and (III) proceed at all, extensive racemisation would undoubtedly accompany both stages, so that for practical purposes the resultant mandelic acid would be optically inactive. Furthermore, these processes must be assumed to continue indefinitely, and by the above mechanism complete racemisation must ultimately result, but in the first experiment quoted (*loc. cit.*, p. 1692), the mandelic acid isolated after 3 weeks had $\alpha_D + 0{\cdot}16°$, $[\alpha]_D + 4{\cdot}7°$, whilst in the second experiment, the mandelic acid isolated after two months at 25° had $\alpha_D + 0{\cdot}31°$, $[\alpha]_D + 5{\cdot}2°$. It does not appear justifiable to base any accurate comparison on the third experiment (*loc. cit.*, p. 1692), in which an optically impure phenylbromoacetic acid ($[\alpha]_D - 70°$) was used, when it was found that the rotation of the solution before isolation of the product was $\alpha_D - 0{\cdot}16°$, and of the mother-liquors after isolation was $\alpha_D - 0{\cdot}45°$; the rotation of

the mandelic acid isolated (= 18·2% of theory) is not recorded, and the rotations of the solutions in this case might well be due to some impurity present initially in the partly racemic phenylbromoacetic acid used. Thus it does not appear that McKenzie and Walker's scheme is correct. Also no explanation is apparent for the almost complete racemisation in stage (I). On the other hand, if the mechanism of the reaction is assumed in the main to be

$$l\text{-PhCHBr}\cdot CO_2' + H_2O(\text{excess}) \xrightarrow{k_1} d\text{-PhCH(OH)}\cdot CO_2'$$
$$l\text{-PhCHBr}\cdot CO_2' + H_2O(\text{excess}) \xrightarrow{k_2} l\text{-PhCH(OH)}\cdot CO_2'$$

where k_1 and k_2 are nearly equal, closer agreement between theory and experiment is obtained. In some cases, according to the conditions, k_1 may be greater than k_2, corresponding with the production of a final dextrorotation, whilst if k_1 is less than k_2, then the solution will remain lævorotatory. This explanation is only tenable if the change of sign of rotation is in accord with the displacement effect as determined by titration, and whereas McKenzie and Walker's experiments showed the displacement to be complete before a final steady rotation value was obtained, the following experimental results did not confirm this.

Reaction between Water and r-*Phenylbromoacetic Acid at* 25°.

Water (250 c.c.) was added to *r*-bromo-acid (1·3438 g. = $N/40$ and 2·5088 g. = $1{\cdot}867N/40$, respectively); in the case of the $N/40$ solution, 72 minutes elapsed before the solution was homogeneous, whilst for the $1{\cdot}867N/40$ solution, 173 minutes were required. These times are reckoned as zero in each set of results. Samples (10 c.c.) were withdrawn and titrated against sodium hydroxide solution ($1{\cdot}011N/40$), with phenolphthalein as indicator. The results are in Table III, k_1 and k_2 being calculated from the usual unimolecular formula.

The theoretical final titres are 19·78 c.c. and 36·93 c.c., respectively. The above data confirm the results of Senter and Tucker (*loc. cit.*, p. 694) and McKenzie and Walker (*loc. cit.*, p. 1693) that the value of the velocity coefficient in $N/40$ solution is appreciably higher than in $1{\cdot}867 \times N/40$ solution (McKenzie and Walker state their results as $k \times 10^{-3}$, whereas they should be $k \times 10^{-2} \times 2{\cdot}3$). This difference is in accord with the different relative concentrations of phenylbromoacetate ions in the two solutions, for, in the reactions

$$\text{PhCHBr}\cdot CO_2H \rightleftharpoons \text{PhCHBr}\cdot CO_2' + H^{\cdot}$$
$$\text{PhCHBr}\cdot CO_2' + H_2O\ (\text{excess}) \longrightarrow \text{PhCH(OH)}\cdot CO_2' + H^{\cdot} + Br'$$
$$\text{PhCH(OH)}\cdot CO_2' + H^{\cdot} \rightleftharpoons \text{PhCH(OH)}\cdot CO_2H,$$

TABLE III.

$N/40$.			$1{\cdot}867 \times N/40$.		
Time.	Titre.	k_1.	Time.	Titre.	k_2.
0 mins.	12·7		0 mins.	25·5	
15	13·3	0·00596	15	26·3	0·00480
30	13·9	0·00626	30	27·0	0·00465
60	14·2	0·00401	60	27·5	0·00318
90	15·0	0·00442	90	28·1	0·00284
120	15·5	0·00425	120	28·6	0·00261
150	15·9	0·00407	150	29·2	0·00258
180	16·2	0·00385	180	29·9	0·00268
210	16·6	0·00388	210	30·4	0·00264
240	16·9	0·00381	240	30·7	0·00251
270	17·1	0·00366	270	31·3	0·00260
330	17·5	0·00350	330	31·8	0·00240
390	17·8	0·00334	390	32·0	0·00213
450	18·1	0·00328	450	32·5	0·00208
510	18·4	0·00330	510	32·9	0·00202
570	18·6	0·00324			
25 hrs.	19·3		24 hrs.	36·0	
47	19·7		45½	37·0	
72	19·7		70½	37·0	

if a_1 is the initial concentration of bromo-acid and α_1 the degree of dissociation, the initial concentration of phenylbromoacetate ion is $a_1\alpha_1$ and therefore the initial rate of reaction is $k\alpha_1 a_1$, whereas the rate in Table III is actually measured by $k_1 a_1$, so that $k = k_1/\alpha_1 = k_2/\alpha_2$ similarly. Now $\alpha_1 = 0{\cdot}3106$ for $N/40$-solution, since the dissociation constant for phenylbromoacetic acid is 0·0035 (Senter and Tucker, *loc. cit.*, p. 692) and $k_1 = 0{\cdot}00406$, taking the mean value in Table III (since the initial values are irregular), so that $k = 0{\cdot}013$. Similarly for $1{\cdot}867N/40$-solution, $\alpha_2 = 0{\cdot}2390$ and $k_2 = 0{\cdot}00284$, giving $k = 0{\cdot}012$.

The important point of difference, however, is that whereas McKenzie and Walker's titration experiment showed the displacement of halogen to be complete after 25½ hours, in the present experiments all the halogen was not displaced in this time, but was complete only after some 50 hours, for the initial rate of reaction falls off rapidly as the reaction proceeds, owing to the accumulation of hydrogen ions in the system.

Reaction between Water and l-*Phenylbromoacetic Acid at* 25°.

The optical kinetic experiment of McKenzie and Walker (*loc. cit.*, p. 1693) was also repeated, but in this case a 4-dcm. tube was used and measurements were made both for the yellow and the green mercury lines. Accordingly 0·3011 g. of *l*-bromo-acid with $[\alpha]^{17°}_{5461}$ − 177° in benzene was dissolved in 30 c.c. of water (= $1{\cdot}867N/40$) at 25°. Solution occupied 62 minutes, and this is shown as zero-time in Table IV. The values of k are calculated for a unimolecular reaction.

TABLE IV.

Time.	$\alpha^{25°}_{5780}$.	k.	$\alpha^{25°}_{5461}$.	k.
0 mins.	−4·25°		−4·67°	
15	−3·98	0·00427	−4·37	0·00428
30	−3·76	0·00397	−4·09	0·00428
45	−3·56	0·00382	−3·87	0·00404
60	−3·29	0·00414	−3·65	0·00397
90	−2·92	0·00409	−3·21	0·00401
120	−2·64	0·00384	−2·85	0·00396
150	−2·34	0·00384	−2·57	0·00382
180	−2·08	0·00382	−2·27	0·00383
210	−1·83	0·00385	−2·03	0·00378
240	−1·67	0·00373	−1·83	0·00371
270	−1·48	0·00373	−1·63	0·00370
330	−1·20	0·00364	−1·32	0·00361
390	−1·00	0·00350	−1·05	0·00358
450	−0·77	0·00355	−0·85	0·00351
570	−0·53	0·00336	−0·55	0·00340
690	−0·33	0·00332	−0·36	0·00328
25 hrs.	+0·04	0·00275	+0·05	0·00265
30½	+0·07		+0·09	
34½	+0·08		+0·10	
49½	+0·12		+0·14	
120	+0·11		+0·14	

The final change in the rotation of the solution is thus to be attributed to the completion of the displacement reaction, and stages (II) and (III) of McKenzie and Walker's scheme become unnecessary. For comparison, the various results in the two papers previously referred to, calculated on the basis of a unimolecular reaction, are summarised in the following table, together with the present results.

Experiment.	k (Titration).	k (Optical).
(1) *l*-Acid, 25°	—	0·00373
r-Acid, 25°	0·00284	—
(2) *l*-Acid, 36·8°	0·0142	0·0161
(3) Sodium salt of *l*-acid, 24·8°	—	0·0166
,, ,, of *r*-acid, 25°	0·0147	—
(4) Sodium salt of *l*-acid, sodium hydroxide, 24·1°	—	0·0179
,, ,, of *r*-acid, sodium hydroxide, 25°	0·0181	—
	0·0175	

In cases (1), (2), and (3), the individual values of k fall off with time, so that the mean values above are calculated over corresponding time intervals. There is a general agreement throughout between the two series of coefficients, but those from the optical measurements are higher than those based on titrations; this difference would agree, as also in the case of the chloro-acid, with a catalytic racemisation of the phenylbromoacetate ion occurring simultaneously with the displacement racemisation. The catalytic racemisation of phenylbromoacetic acid in aqueous acetone solution was clearly demonstrated by McKenzie and Walker (*loc. cit.*, p. 1694). The mechanisms of the conversions of phenylbromoacetic acid and

its sodium salt to mandelic acid and sodium mandelate thus agree with the mechanism above suggested much better than with that advanced previously.

Discussion of Results.

The above results show that the reaction of water with *l*-phenylchloroacetate and *l*-phenylbromoacetate ions yields simultaneously both *l*-mandelate and *d*-mandelate ions by the same simple reaction from the kinetic point of view, the one reagent thus behaving both "normally" and "abnormally" at the same time in this reaction. The production of phenylaminoacetic acids of either sign from a given phenylchloroacetic acid (Senter and Drew, J., 1915, **105**, 638; 1916, **107**, 1091) or phenylbromoacetic acid (Senter and Tucker, J., 1918, **113**, 140) by reaction with ammonia in various solvents is explicable on the above basis, for the relative values of the velocity coefficients will certainly depend on the solvent medium (compare Senter, Drew, and Martin, J., 1918, **113**, 155). In the case of the other conversions similarly studied (Senter, Drew, and Martin, *loc. cit.*; Senter and Ward, J., 1924, **125**, 2137; 1925, **127**, 1847), it would appear probable that the relative values of the two velocity coefficients differ more widely, agreeing with the production of the same isomeride in excess for all solvents studied.

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CLII.—*Substituted Cinnamic Amides and Acids.*

By HAROLD AINSWORTH HARRISON and HAROLD WOOD.

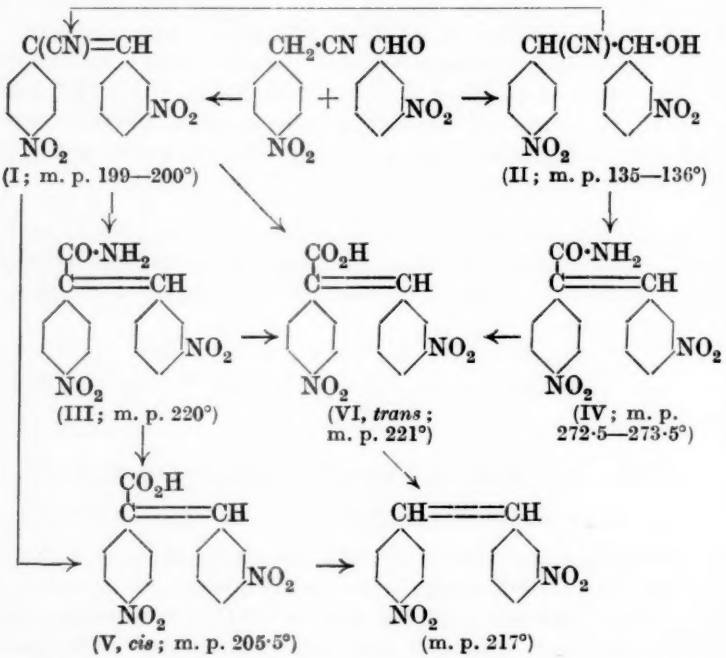
IN a previous paper (this vol., p. 577) the configuration of a 3 : 4′-dinitrochlorostilbene resulting from the elimination of one molecule of hydrogen chloride from the stilbene dichloride was determined by the fact that sulphuric acid converted it into 4-nitrophenyl 3-nitrobenzyl ketone. The constitution of this ketone was deduced from its non-identity with the isomeric 3-nitrophenyl 4-nitrobenzyl ketone obtained by oxidation of the intermediate aldol compound isolated during the condensation of *p*-nitrophenylacetic acid with *m*-nitrobenzaldehyde and therefore having the structure

$$(p)NO_2\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot C_6H_4\cdot NO_2(m).$$

Another synthesis of 4-nitrophenyl 3-nitrobenzyl ketone [from

3 : 4′-dinitro-α-phenylcinnamamide, utilising Weerman's modification of the Hofmann reaction (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, **10**, 308; *Annalen*, 1913, **401**, 1; *Rec. trav. chim.*, 1917, **37**, 1)], which confirmed the foregoing conclusions, is now described.

When *p*-nitrophenylacetonitrile and *m*-nitrobenzaldehyde are combined, with sodium ethoxide or piperidine as condensing agent, according to the method of Remse (*Ber.*, 1890, **23**, 3135), 3 : 4′-dinitro-α-phenylcinnamonitrile (I) and 3 : 4′-*dinitro*-β-*hydroxy*-α-*phenyldihydrocinnamonitrile* (II) are formed in about equal quantities. Neither Remse (*loc. cit.*) nor Freund (*Ber.*, 1901, **34**, 3107), both of whom carried out this same experiment, mentions the formation of (II), their sole product being (I).* The aldol compound (II) may be converted into (I) by the action of sulphuric acid, pyridine or piperidine.



Two quite different stereoisomeric *amides* (III and IV) are produced when (I) and (II) are hydrolysed with sulphuric acid. Amide (IV) on further hydrolysis with sulphuric acid yields only one acid (VI), but amide (III) under the same conditions gives a mixture of

* From *o*-nitrobenzaldehyde and *p*-nitrophenylacetonitrile, however, Freund (*loc. cit.*) did isolate two compounds analogous to (I) and (II) above.

(V) and (VI); the same mixture is also formed when the nitrile (I) is directly hydrolysed to the acid stage. When amide (III) is hydrolysed with nitrous acid, however, acid (V) is almost the sole product.

The two *acids* (V) and (VI) can be separated, by Stoërmer and Prigge's method (*Annalen*, 1915, **409**, 20), by taking advantage of their widely differing strengths. Acid (VI) is the weaker, and from analogy with Stoërmer's results (see also Stoërmer and Voht, *ibid.*, 1915, **409**, 36) it is provisionally called the "*trans*" modification; the term applies to the relative positions of the phenyl and carboxyl groups, and not to the two phenyl groups.

Acids (V) and (VI) can both be decarboxylated by heating with piperidine, and yield the same form of 3 : 4′-dinitrostilbene.

Experimental.

3 : 4′-*Dinitro*-β-*hydroxy*-α-*phenyldihydrocinnamonitrile* (II).—When the condensation of *p*-nitrophenylacetonitrile and *m*-nitrobenzaldehyde in presence of piperidine or sodium ethoxide was allowed to proceed for only a few hours the product contained not only 3 : 4′-dinitro-α-phenylcinnamonitrile (I), m. p. 199—200° after recrystallisation from acetic acid (Remse and Freund give m. p. 195°), but also an equal amount of the intermediate *aldol* (II), which was isolated from the alcoholic mother-liquors, the total yield of the two nitriles being 85—90%. After many recrystallisations from acetic acid the aldol was obtained in yellow, crystalline aggregates, m. p. 135—136° (Found: C, 57·2; H, 3·6. $C_{15}H_{11}O_5N_3$ requires C, 57·5; H, 3·5%). It is easily soluble in pyridine, nitrobenzene, acetone, or ethyl acetate, less soluble in alcohol or benzene, and somewhat sparingly soluble in chloroform, carbon tetrachloride, or light petroleum. (II) can be converted into (I) by dissolution in cold concentrated sulphuric acid, by dissolving it in hot pyridine and keeping the solution for several days, or by keeping the crude reaction mixture (in presence of alcoholic piperidine) for a week.

The Two Stereoisomeric Forms of 3 : 4′-*Dinitro*-α-*phenylcinnamamide* (III and IV).—Each of the nitriles (I) and (II) (20 g.) was carefully dissolved in warm concentrated sulphuric acid (340 c.c.), water (46 c.c.) added, and the mixture heated on the steam-bath for 6 hours. When cold, the solution was poured into 2 litres of water, and the precipitated amide washed with hot dilute ammonia and with water (yield 96—99%). The *amide* (III), obtained from (I), separated from acetic acid in almost colourless needles, m. p. 220° (Found: C, 57·4; H, 3·6. $C_{15}H_{11}O_5N_3$ requires C, 57·5; H, 3·5%). It is sparingly soluble in the usual organic solvents, and is not hydrolysed to the acid by boiling with hydrochloric acid for 2 days. The higher-melting form of the *amide* (IV), obtained from

(II), is even less soluble than (III) in organic solvents. It separates from acetic acid in microscopic prisms and from nitrobenzene in thin plates, m. p. 272·5—273·5° (Found: C, 57·2; H, 3·9%).

Conversion of the Amide (III) into 4-Nitrophenyl 3-Nitrobenzyl Ketone.—A paste of the finely powdered amide (20 g.) and boiling methyl alcohol was cooled and added, with shaking, to a solution of sodium hypochlorite during 1 hour. The mixture was then heated at 80° for ½ hour, much unchanged amide filtered off, the warm liquor acidified with dilute sulphuric acid, and the dark brown precipitate repeatedly crystallised from alcohol (charcoal). The slightly brown needles thus obtained melted at 132°, alone or mixed with 4-nitrophenyl 3-nitrobenzyl ketone. The yield was exceedingly poor, but the constitution of the ketone was proved.

cis *and* trans *Forms of* 3 : 4′-*Dinitro-α-phenylcinnamic Acid* (V and VI).*—Amide (III) (17 g.) was boiled with a mixture of strong sulphuric acid, acetic acid, and water (125 c.c. of each) for 2 days, the product poured into water, and the filtered solid digested with hot sodium carbonate solution; the addition at 95° of a slight excess of acetic acid precipitated, in 48% yield, the weaker "*trans*" acid (VI), which crystallised from ethyl acetate in large, pale yellow prisms, m. p. 221° (Found: C, 57·2; H, 3·2; equiv., 316. $C_{15}H_{10}O_6N_2$ requires C, 57·3; H, 3·2%; equiv., 314). This isomeride is much less soluble than (V) in methyl alcohol or ethyl acetate.

From the hot filtrate after removal of acid (VI), most of the stronger "*cis*" acid (V) separated out, mixed with a little (VI), and addition of hydrochloric acid to the cold filtrate increased the yield to 36%. After two crystallisations from acetic acid (V) was obtained in rosettes of slightly brown needles, m. p. 205·5° (Found: C, 56·9; H, 3·3%; equiv., 312). It is readily soluble in hot methyl or ethyl alcohol, or acetic acid, and is moderately soluble in cold ethyl acetate.

From the nitrile (I), by hydrolysis under the above conditions, 32% of acid (VI) and 38% of acid (V) were obtained.

Hydrolysis of amide (IV) during 3 days led to the formation of acid (VI) in 77% yield. No acid (V) was discovered, the cold filtrate after removal of (VI) by acetic acid remaining quite clear on addition of hydrochloric acid.

Hydrolysis of Amide (III) with Nitrous Acid.—To a solution of amide (III) in cold concentrated sulphuric acid an excess of sodium nitrite was added, with water-cooling. After 2 days, the solution was diluted with water and kept for a week, a little more nitrite being added occasionally. The solid was removed, washed, and

* For a description of the piperidine salts of these two acids, see this vol., p. 580.

thoroughly digested on the filter with hot sodium carbonate solution. Acetic acid was added to the boiling filtrate in slight excess, and the solution again filtered hot to remove a very small amount of precipitate (VI). On cooling, the filtrate deposited acid (V) in 80% yield.

Decarboxylation of Acids (V) and (VI).—The acid (3 g.) was dissolved in boiling acetone, piperidine (½ c.c.) added, and the acetone distilled off. The intimate mixture thus obtained was heated at 225° for ½ hour, and, after cooling, the resinous product was washed several times with boiling acetone and finally recrystallised from acetic acid, when it melted at 216°, either alone or mixed with an authentic specimen of 3 : 4′-dinitrostilbene (for which see this vol., p. 580). The yields from acids (V) and (VI) were respectively 27% and 32%.

In conclusion, one of us (H. W.) desires to express his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant, and the other (H. A. H.) to the Chemical Society Research Fund Committee for a grant for materials. We also thank Professor Lapworth for his continued interest and advice.

THE UNIVERSITY, MANCHESTER. [*Received, January 30th*, 1926.]

CLIII—*The Chemistry of the Glutaconic Acids. Part XIX. A Consequence of Mobility.*

By JOHN PACKER and JOCELYN FIELD THORPE.

THE mobility of the hydrogen atom in the three-carbon system

$$HC{\cdot}C{:}C \rightleftharpoons C{:}C{\cdot}CH,$$

so far as it has yet been investigated, reaches its maximum in glutaconic acid, causing this substance to exist in only one form, the postulated " normal " form to which has been ascribed the tentative constitution $CO_2H{\cdot}CH{\cdot}CH(H){\cdot}CH{\cdot}CO_2H$.

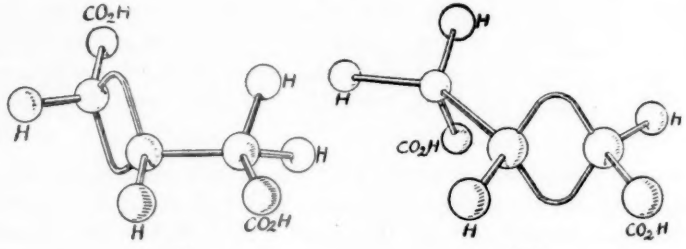
If the corresponding unsaturated formulæ be set up on the models, drawings of which are shown in Fig. 1, it will be found that this mobility may or may not involve a change from the hypothetical *cis-* (I) to the *trans-* (II) form and *vice versa*, depending on the spatial relationship of the methylene hydrogen atoms to the double bond at the time of change.

While this fact is, in itself, no argument for or against the " normal " form, yet it supplies certain explanations and deductions which are of fundamental importance in connexion with the chemistry of these substances.

It is certainly paradoxical that, whilst the two hydrogen atoms

of the methylene group are of equal value owing to the occurrence of free rotation about the single bond, they should have different values when used in bringing about the three-carbon change. But it must be remembered that the positions of the constituent atoms in space are determined by the tendency for like groups to take up positions as remote as possible from one another, a tendency which the molecule can satisfy owing to its power of free rotation about the single bond.

FIG. 1.



(I) (II)

In the case of glutaconic acid, where it is immaterial on which side of the central carbon atom the double bond is placed, the tautomeric change would be expected, in the case of the *trans*-form to take place mainly without alteration in stereochemical configuration, and in the case of the *cis*-form to result mainly in conversion into the *trans*-form. In those derivatives of glutaconic acid in which substituting groups are attached to the α, β, or γ carbon atom and which may in consequence exist theoretically in more forms, the necessary alterations in the stable positions of the atoms in space may lead to differences in the tendency of the *cis*- and *trans*-forms to be converted into one another by the tautomeric change.

Certain deductions given below render it probable that valuable evidence will be obtainable on these lines regarding the existence or non-existence of the postulated " normal " form. Experiments on this point are now in hand, but it is thought desirable to publish this new point of view at once, because it offers an explanation as to why both forms of, for example, the β-methylglutaconic acids readily yield anhydrides.

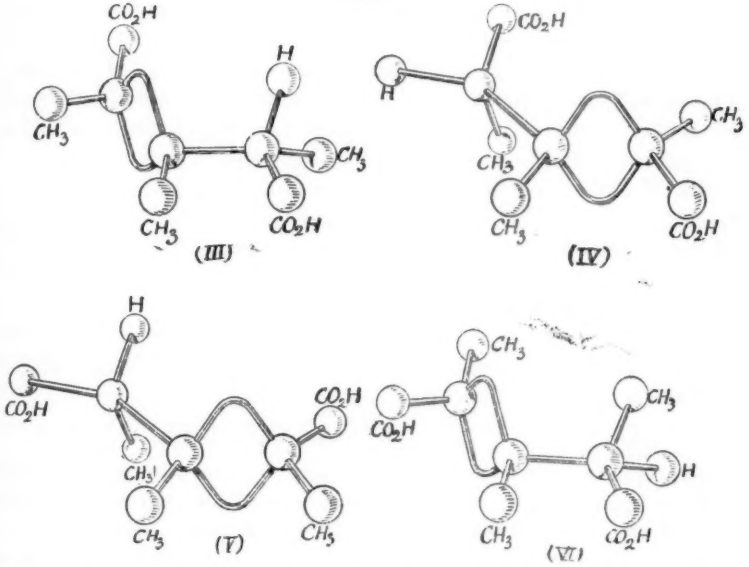
The argument has been used by us that the ready formation of the hydroxy-anhydride from both forms of β-methylglutaconic acid favours the assumption of the " normal " form rather than the *cis*- and *trans*-configuration, because in the analogous case of non-mobile systems, for example, αα-dimethylglutaconic acid, $CO_2H{\cdot}C(CH_3)_2{\cdot}CH{:}CH{\cdot}CO_2H$, the *trans*-form gives no anhydride. It is evident, however, from a study of the models, which are similar

to those for glutaconic acid, that the formation of the hydroxy-anhydride may be preceded by a change of configuration and hence the relative ease of formation of the anhydride from the *trans*- and *cis*-forms is seen to depend on the mobility of the tautomeric system under the conditions of dehydration.

The authors do not wish to call into question the existence of the "normal" form, which is supported by a number of experimental facts, but they desire to point out that:

A. Assuming glutaconic acid to be the stable *trans*-form, it follows that the formation of the hydroxy-anhydride must take

FIG. 2.



place through the *cis*-modification, the inability to isolate the *cis*-form of the acid by hydration of the hydroxy-anhydride being due to the mobility of the system. The existence of two forms of β-methylglutaconic acid, each giving the same hydroxy-anhydride with equal readiness, is due to the same mechanism, but in this case the order of mobility is lower and hence the *cis*-modification can be isolated by hydrating the hydroxy-anhydride under special conditions.

B. In such cases as the αγ-dimethyl- and αβγ-trimethyl-glutaconic acids, the theoretically possible *cis*- and *trans*-forms should be capable of resolution into optically active forms, so that, for example, the four forms of the αβγ-trimethylglutaconic acids depicted in Fig. 2 should be capable of existence as well as the "normal" form

$CO_2H{\cdot}C(CH_3){\cdot}C(CH_3)(H){\cdot}C(CH_3){\cdot}CO_2H$. It will be seen that the tautomeric changes may result in the following transformations

$$\begin{array}{ccc} d\text{-}cis\ (\mathrm{III}) & \rightleftharpoons & d\text{-}trans\ (\mathrm{IV}) \\ \Updownarrow & & \Updownarrow \\ l\text{-}cis\ (\mathrm{V}) & \rightleftharpoons & l\text{-}trans\ (\mathrm{VI}) \end{array}$$

but when the tendency of like groups to take up positions as far apart as possible is also considered the following deductions can be made :

(i) The two enantiomorphous *cis*-forms (III) and (V) will tend to pass into the correspondingly active *trans*-forms (IV) and (VI) rather than into each other, unless the change is arrested at the intermediate " normal " form.

(ii) The two enantiomorphous *trans*-forms (IV) and (VI) will show a greater tendency to interconversion (racemisation) than in the case of the *cis*-forms, and this change may take place to the practical exclusion of transformation into the *cis*-forms.

(iii) If the stable form of the acid is the *trans*-form, it will be capable of resolution into optically active forms which will be distinct from the active forms of the *cis*- (labile) acid ; inability to resolve the stable form would be evidence for the " normal " constitution.

C. In the case of α- and αβ-substituted glutaconic acids the structural isomerides (VII) and (VIII) are theoretically possible as well as the " normal " form

(VII.) $CO_2H{\cdot}CR^1{:}CR^2{\cdot}CH_2{\cdot}CO_2H$ $CO_2H{\cdot}CR^1H{\cdot}CR^2{:}CH{\cdot}CO_2H$ (VIII)

and each may exist in *cis*- and *trans*-forms. The two forms of (VII) will be incapable of resolution into optically active forms, whilst the two forms of (VIII) will be capable of such resolution under conditions not leading to tautomeric mobility. This should afford an experimental means of determining the position of the double bond in these unsaturated forms.

These isomeric forms are theoretically interconvertible by tautomeric change according to the scheme :

$$\begin{array}{ccc} i\text{-}cis & \rightleftharpoons & \left.\begin{matrix} d\text{-} \\ l\text{-} \end{matrix}\right\} trans \\ \Updownarrow & & \Updownarrow \\ \left.\begin{matrix} d\text{-} \\ l\text{-} \end{matrix}\right\} cis & \rightleftharpoons & \text{-}\ rans \end{array}$$

and a study of the models in these cases leads to the following conclusions :

(i) Where R^1 and R^2 are positive groups, the *trans*-forms will be more stable than the *cis*-forms.

(ii) Where R^2 is a negative group (*e.g.*, C_6H_5), the relative stability of the *cis*-forms will be increased.

D. The reduction in mobility of the glutaconic system brought about by the substitution of various groups for hydrogen atoms, and the consequent increase in stability of the labile unsaturated forms, can be explained by an application of Thorpe and Ingold's theory of the influence of attached groups on the carbon tetrahedral angle; for the effect of such groups is obviously to reduce the strain in the double bond or two-carbon ring.

The effect of a group in the β-position will be to stabilise both the αβ- and βγ-unsaturated forms, whilst the effect of a group in the α-position will be greater in stabilising the αβ- than the βγ-unsaturated form, so that in general a group in the β-position will have a greater effect in retarding the mobility of the system than will the same group in the α-position. Hence in the case of α- and αβ-substituted acids, the αβ-unsaturated forms (VII) should be more stable than the βγ-unsaturated forms (VIII).

In the case of β-phenyl-α-methylglutaconic acid one stable and three labile forms are known. To the *cis*- and *trans*-labile forms of Thorpe and Wood have been assigned the αβ-, and to the labile form of Feist the βγ-unsaturated structure. If these constitutions are correct, the above considerations favour the "normal" structure for the stable form of the acid, since the only other possible structure is that of the βγ-unsaturated *trans*-form, which would be expected to be relatively unstable.

An examination of these acids from the above points of view has been commenced in the hope of thus throwing further light on their constitutions.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, February 4th*, 1926.]

CLIV.—*Selective Solvent Action. Part V. Salting in.*

By ROBERT WRIGHT.

THE mutual lowering of solubility which takes place when an electrolyte and an organic substance are dissolved together in water has been the subject of many investigations (Rothmund, "Löslichkeit und Löslichkeitsbeeinflussung"), and is the basis of the process of "salting out" when an organic compound is driven out of aqueous solution by the addition of a salt. What may be termed "salting in" is the reverse phenomenon, that is, a mutual increase

in solubility of electrolyte and organic compound when added to the same solvent, which in this case is not pure water but aqueous alcohol.

In former papers (J., 1922, **121**, 2252; 1923, **123**, 2493; 1925, **127**, 2335) it was shown that the addition of a semi-solute to a mixed solvent raised both the vapour pressure and the freezing point of the constituent in which it was insoluble. Thus sodium chloride (or other salt) raised the alcohol vapour pressure of aqueous alcohol, whilst water raised the freezing-point of benzene in an alcohol–benzene mixture. It was pointed out that this might be explained on the solvate hypothesis: in the alcohol–benzene mixture, we have complexes formed between the two constituents; water, when added, competes with the benzene for the alcohol, forming water–alcohol solvates and decomposing some of the alcohol–benzene solvates, thus leaving the solution richer in free benzene and therefore with a higher freezing-point and benzene vapour pressure.

A corresponding effect might be expected in the case of solubility. The addition of salt to aqueous alcohol should form salt hydrates with a consequent increase in the free alcohol present and a corresponding increase in solvent power for benzene or other organic substances. Conversely, the presence of benzene should increase the solvent power of the mixed solvent for a water-soluble solute.

This effect can readily be demonstrated in a qualitative manner. To 100 c.c. of 50% alcohol, benzene is added 1 c.c. at a time until the solution turns turbid; if sodium chloride is now added to the turbid mixture, the liberated alcohol (due to the removal of water for the formation of salt hydrates) will dissolve the excess of benzene and cause the solution to become clear.

Quantitative determinations of this increase of solubility in 50% (by weight) aqueous alcohol have been made with benzene, carbon tetrachloride, and methyl salicylate as alcohol-soluble solutes, and with sodium chloride, sodium nitrate, potassium chloride, potassium bromide, and potassium nitrate as water-soluble salts. It will be noted that none of the salts crystallises with water of crystallisation.

In the method employed, about 12 g. of the aqueous alcohol were weighed in a stoppered tube and excess of salt was added. The benzene, or other organic compound, was weighed in a weight burette and added to the solution in the tube, in small quantities, until turbidity was produced, the quantity of benzene thus added being found by a second weighing. The turbid mixture was shaken in a thermostat at 20° $\pm$ 0·1° for 6 hours until the solution was saturated with both solutes. About 2 c.c. of the solution were then weighed in a stoppered bottle and the salt was estimated by evaporation to dryness and weighing. Since the proportion of benzene to

aqueous alcohol in the solution is known, the percentage of both salt and benzene dissolved in the aqueous alcohol can be calculated and compared with the percentage when only one solute—benzene or salt—is present. The results obtained are in Tables I and II, and it will be seen that the solubility of each semi-solute is increased by the presence of the other, the increase being considerable in the case of the organic compound.

TABLE I.

Solubilities of organic compounds in 100 g. of 50% aqueous alcohol saturated with different salts at 20°.

Salt present.	None.	NaCl.	$NaNO_3$.	KCl.	KNO_3.	KBr.
Benzene	5·8	9·6	9·5	6·7	6·4	7·8
Carbon tetrachloride...	6·4	13·4	8·2	9·9	7·1	9·9
Methyl salicylate	6·2	8·2	8·1	7·2	6·9	7·9

TABLE II.

Solubilities of salts in 100 g. of 50% aqueous alcohol saturated with organic compounds at 20°.

Organic compound.	None.	Benzene.	Carbon tetrachloride.	Methyl salicylate.
Sodium chloride	9·8	10·6	10·7	10·2
„ nitrate	19·4	21·2	20·8	20·4
Potassium chloride	6·0	6·5	6·8	6·2
„ nitrate	3·7	3·9	3·8	3·8
„ bromide	16·4	17·4	17·4	17·3

Four determinations of the solubility of the salt were made in each case, and the results seldom differed by more than one unit in the first decimal place. The solubility of the organic substance was less accurate and, since it was determined by the appearance of turbidity, was always too great, the error being about three units in the decimal place. This error is of less importance in that the increase in solubility of the organic substance is always much greater than that of the salt.

A somewhat more accurate investigation was carried out in the case of benzene and sodium chloride. The solubility of benzene in 50% alcohol was determined at a series of temperatures by adding a weighed quantity of benzene to a definite weight of the solvent and raising the temperature until the turbidity disappeared. A second series was also carried out after 5% of sodium chloride had been added to the aqueous alcohol. The results—which are in Table III—when plotted give two curves practically parallel to each other. The solubility of sodium chloride in 50% alcohol containing small quantities of benzene was also determined, the quantity of benzene being less than that which would produce turbidity. The results are in Table IV.

TABLE III.

Solubility of benzene in 50% aqueous alcohol.		Solubility of benzene in 50% alcohol with 5% NaCl.	
% Benzene.	Temp.	% Benzene.	Temp.
4·57	11·2°	5·80	9·1°
4·78	13·2	6·10	11·8
5·05	15·5	6·39	14·2
5·30	18·0	6·76	16·7
5·61	20·2	7·23	19·2
5·97	22·6	7·57	21·3

TABLE IV.

Solubility at 20° of sodium chloride in 100 g. of 50% aqueous alcohol containing a varying percentage of benzene.

% Benzene	0·00	1·91	4·10	5·34	7·95
% Sodium chloride	9·80	9·86	9·95	10·10	10·35

As is well known, the addition of potassium carbonate to aqueous alcohol causes the formation of two liquid phases, the greater concentration of the salt being found in the lower (aqueous) layer. The amount of carbonate required to produce turbidity increases with the amount of water present, hence a system which contains just sufficient carbonate to produce turbidity can be cleared by a slight addition of water. This small amount of water can be produced by the desolvation of aqueous alcohol caused by the addition of benzene. For example, if about 0·05 g. of potassium carbonate be dissolved in 2 c.c. of water and 10 c.c. of alcohol be added, a turbid mixture will result, which can be cleared by the addition of either a little water or a larger amount of benzene. A large excess of benzene will again produce turbidity, the benzene forming a layer on top of the aqueous alcohol. Also, if the system contains a larger proportion of carbonate, it is possible, by the addition of benzene, to produce a system of three liquid phases, the benzene and the aqueous salt solution being separated by a layer of aqueous alcohol. That potassium carbonate—like other salts—increases the solubility of benzene in aqueous alcohol is shown by the results given in Table V.

TABLE V.

Solubility at 20° of benzene in 100 g. of aqueous alcohol containing a varying percentage of potassium carbonate.

% Potassium carbonate	0·00	1·12	1·67	2·18	2·48	2·68*	2·86
% Benzene	5·8	6·4	6·5	7·1	7·3	7·6	8·0

* Two phases separate.

It is evident from the results shown that with 50% aqueous alcohol there is a mutual increase in solubility of the two types of semi-

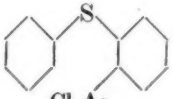
solute when they are present together. It has not been considered advisable to attempt to assign any definite degree of solvation to the semi-solutes, as the number of equilibria involved would render any such calculation of very doubtful value.

GLASGOW UNIVERSITY. [*Received, March 12th*, 1926.]

CLV.—10-*Chlorophenthiarsine, and its Rate of Formation from* o-*Phenylthiolphenyldichloroarsine.*

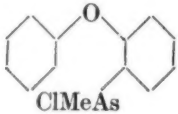
By ELWYN ROBERTS and EUSTACE EBENEZER TURNER.

IN continuation of previous work (Roberts and Turner, J., 1925, **127**, 2004), o-*phenylthiolphenyldichloroarsine* (I) has been prepared, and its rate of conversion into 10-*chlorophenthiarsine* (II) determined. Whereas *o*-phenoxyphenyldichloroarsine undergoes nearly 60% conversion into the ring compound, the sulphur analogue undergoes only about 20% conversion under the same conditions, *i.e.*, when heated at 200° in a current of carbon dioxide.



(I.)

(II.)



(III.)

A further comparison has been made between *o*-phenoxyphenyldichloroarsine and o-*phenoxyphenylmethylchloroarsine* (III) from the same point of view. The chloroarsine is even more stable towards heat than the above phenylthiol compound, undergoing in 6 hours at 200° only about 10% of the possible loss of hydrogen chloride. Moreover, side reactions appear to occur, and it has not been found possible to detect the presence of the expected 10-methylphenoxarsine in the product of decomposition. The latter, when treated with methyl iodide, afforded a little 10-iodophenoxarsine, but no 10 : 10-*dimethylphenoxarsonium iodide*. This substance has been prepared, for purposes of comparison, by treating with methyl iodide the product of interaction of magnesium methyl iodide and 10-chlorophenoxarsine.

It has been pointed out (Turner and Sheppard, J., 1925, **127**, 544) that arsenic trichloride and diphenyl ether do not interact in absence of aluminium chloride. It seemed possible that this might be due to the low boiling point of the mixture, which is well below the temperature at which phenoxyphenyldichloroarsine undergoes conversion into the chlorophenoxarsine. It has, however, been

found that a mixture of phenyldichloroarsine and diphenyl ether boils unchanged at 250—260°, so that the ring closures in question are evidently determined more by collision effects than by those of activation due to increase of temperature.

EXPERIMENTAL.

o-*Nitrodiphenyl Sulphide.*—This substance, previously obtained by Mauthner (Ber., 1906, **39**, 3593), is more conveniently prepared by the following method: Potassium hydroxide (61 g.; 1 mol.) was dissolved in 5 c.c. of water, 120 g. (1 mol.) of thiophenol, and then 173 g. (1 mol.) of *o*-chloronitrobenzene and 8 g. of copper bronze were added. The mixture was heated at 170—185° for 2 hours after the initial vigorous reaction had subsided. The cooled product was extracted with carbon tetrachloride, the extract washed successively with alkali and water, and dried over calcium chloride. The solvent was removed, and the residue distilled under diminished pressure. In this manner, 138 g. of *o*-nitrodiphenyl sulphide were obtained, b. p. 210°/15 mm. Crystallisation from light petroleum removed traces of a disulphide, the pure nitro-compound having m. p. 79° (Mauthner gives 77°).

o-*Aminodiphenyl Sulphide.*—The foregoing nitro-compound was reduced with iron, water and ferric chloride (Roberts and Turner, *loc. cit.*). A little thiophenol is formed during the reduction, which proceeds less vigorously than in the case of *o*-nitrodiphenyl ether, but affords not less than an 85% yield of the amine hydrochloride.

o-*Phenylthiolphenylarsinic Acid.*—The pure acid was obtained in 12% yield by the method used for the preparation of phenoxyphenylarsinic acids, and crystallised from alcohol in irregular plates, m. p. 192—194° (Found: As, 24·0. $C_{12}H_{11}O_3SAs$ requires As, 24·2%). The acid is sparingly soluble in water, and was not converted into the corresponding phenthiarsinic acid when heated with concentrated sulphuric acid, no doubt owing to sulphonation.

o-*Phenylthiolphenyldichloroarsine.*—The preceding arsinic acid, when reduced by the usual process, afforded the crude dichloroarsine as a dark oil, which was purified by conversion into the corresponding oxide (see below), the latter then being reconverted into the dichloroarsine. The latter was thus obtained as a pale yellowish-brown, viscous oil (Found: Cl, 21·3. $C_{12}H_9Cl_2SAs$ requires Cl, 21·5%). (Traces of the carbon tetrachloride used for the extraction of the pure dichloroarsine were removed by gently heating the substance under diminished pressure for a few minutes.)

o-*Phenylthiolphenylarsenious oxide* separates from benzene in small, white, irregular rhombs, m. p. 187—189° (Found: As, 26·5. $C_{12}H_9OSAs$ requires As, 27·2%).

Conversion of o-*Phenylthiolphenyldichloroarsine into* 10-*Chlorophenthiarsine.*—When heated at 200° under the conditions previously described in connexion with the conversion of the phenoxyphenyldichloroarsines into the corresponding chlorophenoxarsines, *o*-phenylthiolphenyldichloroarsine underwent the following course of decomposition :

Time (hours)	1	2	3	4	5	6
% decomposition	2·2	4·5	7·2	10·2	13·6	17·2

The heating was actually allowed to continue for 24 hours; the product, almost solid when cold, then readily crystallised from light petroleum (b. p. 80—100°) in sulphur-yellow, rhombohedral masses, apparently consisting of rectangular plates, m. p. 129—130° (Found : Cl, 12·1. $C_{12}H_8ClSAs$ requires Cl, 12·1%).

o-*Phenoxyphenylmethylchloroarsine.*—*o*-Phenoxyphenyldichloroarsine (19 g.) was dissolved in alcohol containing a little acetone, and a solution of 12 g. of sodium hydroxide in 90 c.c. of water added. The mixture was cooled to 40°, and 8 c.c. of methyl iodide were added slowly. The initial reaction over, the whole was left over-night, when a pale yellow oil separated. The alcohol and acetone were distilled off and the residue was acidified with concentrated hydrochloric acid (25 c.c.); a gummy solid then separated. Potassium iodide (19 g.) was added, and the warmed mixture saturated with sulphur dioxide. The dark red, oily iodoarsine so obtained was converted into the corresponding oxide, and then, by the usual process, into the chloroarsine, which was obtained as a brownish-yellow, viscous oil; it contained a little dichloroarsine (Found : Cl, 13·8. $C_{13}H_{12}OClAs$ requires Cl, 12·1%).

When this substance was heated at 200° in a current of dry carbon dioxide under the same conditions as before, the course of decomposition was as follows :

Time (hours)	1	2	3	4	5	6
% decomposition	2·5	3·9	5·0	6·4	7·8	9·9

Some methyl chloride was also evolved, and when the decomposition had proceeded for 24 hours, methyl iodide was added to the cooled residue. From the product so obtained, a very small quantity of 10-iodophenoxarsine, m. p. 144°, was isolated (Found : I, 33·8. Calc. : I, 34.3%).

10 : 10-*Dimethylphenoxarsonium Iodide.*—Finely-powdered 10-chlorophenoxarsine (4 g.) was added gradually to an ethereal solution of magnesium methyl iodide (twice the theoretical amount). It dissolved immediately with evolution of heat, and formation, locally, of a yellow coloration. As soon as it had all been added, the mixture was decomposed by addition of water and then dilute

hydrochloric acid, the ethereal layer separated, washed once with water, dried over sodium sulphate, filtered, and then treated with methyl iodide. After most of the ether had been evaporated, solid separated, which, after crystallisation from alcohol, formed colourless prisms, m. p. 207° (with effervescence) (Found: I, 31·1. $C_{14}H_{14}OIAs$ requires I, 31·7%). The tedious method adopted by Lewis, Lowry, and Bergeim (*J. Amer. Chem. Soc.*, 1921, **43**, 890) and by Aeschlimann (J., 1925, **127**, 811) does not appear to be necessary in the interaction between Grignard reagents and chlorophenoxarsine.

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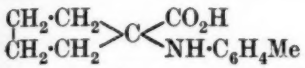
CLVI.—*Some Reactions of* 1-p-*Toluidino*cyclo*pentane*-1-*carboxylic Acid. A New Carbazole Synthesis.*

By STEPHEN HELLICAR OAKESHOTT and SYDNEY GLENN PRESTON PLANT.

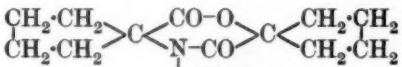
THE reaction whereby 1-anilino*cyclo*pentane-1-carboxylic acid, on fusion with a mixture of sodium ethoxide and potassium hydroxide, gives carbazole (Plant and Facer, J., 1925, **127**, 2037), may follow one of two courses: either the *cyclo*pentane ring may open and form with the carboxyl group the second benzene nucleus of carbazole, or, alternatively, the carbazole may be produced entirely from the anilino-group. It is possible to decide this point by an investigation of 1-*p*-toluidino*cyclo*pentane-1-carboxylic acid (I), which, if the former view is correct, ought to give 3-methylcarbazole as opposed to 3 : 6-dimethylcarbazole, in accordance with the latter view, on fusion under the same conditions.

We have now condensed *p*-toluidine with *cyclo*pentanone cyanohydrin and have converted the 1-p-*toluidino*-1-*cyano*cyclo*pentane* so obtained into the corresponding *amide*, which can be hydrolysed to 1-p-*toluidino*cyclo*pentane*-1-*carboxylic acid*. On heating this acid with a mixture of sodium ethoxide and potassium hydroxide, 3-methylcarbazole was obtained. Its identity was established by careful comparison of the substance obtained and its picrate with 3-methylcarbazole and 3 : 6-dimethylcarbazole, which we find can be obtained most conveniently by oxidising the corresponding methyl derivatives of tetrahydrocarbazole with sulphur, and their respective picrates. It seems clear now that the production of carbazole from 1-anilino*cyclo*pentane-1-carboxylic acid involves the enlargement of the carbocyclic system, probably by absorption of

the carboxyl group. A further investigation of this reaction has shown that it proceeds quite as well in the absence of sodium ethoxide and that the sodium or potassium salt of the acid can be used.



(I.)



(II.)

1-*p*-Toluidino*cyclo*pentane-1-carboxylic acid is comparatively unstable and loses *p*-toluidine and water on heating above its melting point with the formation of the *lactone* of 1-1′-*hydroxy*cyclo*pentane*-1′-*carboxylyl*-p-*toluidino*cyclo*pentane*-1-*carboxylic acid* (II), showing a behaviour similar to that of 1-anilino*cyclo*pentane-1-carboxylic acid in this respect.

EXPERIMENTAL.

1-p-*Toluidino*-1-*cyano*cyclo*pentane*.—*cyclo*Pentanone cyanohydrin will condense with *p*-toluidine when a solution of these substances in benzene is boiled for 12 hours, but conditions similar to those used by Walther and Hübner (*J. pr. Chem.*, 1916, **93**, 124) for the preparation of 1-anilino-1-cyano*cyclo*hexane were found to be more convenient. To a solution of *cyclo*pentanone (21 g.) and *p*-toluidine (27 g.) in glacial acetic acid (100 c.c.), cooled in ice, potassium cyanide (18 g.), dissolved in a little water, was added. 1-p-*Toluidino*-1-*cyano*cyclo*pentane* separated in good yield and was washed with water. It crystallised from low-boiling petroleum in colourless needles, m. p. 55° (Found : N, 14·2. $C_{13}H_{16}N_2$ requires N, 14·0%). The *nitrosoamine*, prepared from an alcoholic solution of the nitrile, dilute hydrochloric acid, and aqueous sodium nitrite, separated from methyl alcohol in yellow prisms, m. p. 58°.

A solution of 1-*p*-toluidino-1-cyano*cyclo*pentane in cold sulphuric acid was kept for 2 days, poured on to ice and the mixture made alkaline with ammonia; the *amide* of 1-p-*toluidino*cyclo*pentane*-1-*carboxylic acid* was then precipitated. It separated from aqueous methyl alcohol in colourless plates, m. p. 120°. Its *nitrosoamine*, prepared by adding sodium nitrite to the amide dissolved in alcoholic hydrochloric acid, separated from aqueous methyl alcohol in yellow needles, m. p. 132°.

1-p-*Toluidino*cyclo*pentane*-1-*carboxylic Acid*.—A mixture of the crude amide and concentrated hydrochloric acid was boiled under reflux for 2 hours, evaporated to dryness, the residue treated with an excess of aqueous sodium hydroxide, and the solution boiled and filtered. The addition of glacial acetic acid to the cold filtrate precipitated 1-p-*toluidino*cyclo*pentane*-1-*carboxylic acid*, which separated from benzene–petroleum in colourless leaves, m. p. 144°

(Found : N, 6·6. $C_{13}H_{17}O_2N$ requires N, 6·4%). 1-*p*-Toluidino-*cyclo*pentane-1-carboxylic acid is soluble in dilute aqueous sodium hydroxide and in dilute hydrochloric acid and gives a *nitrosoamine*, which separates from aqueous methyl alcohol in pale yellow plates, m. p. 114° (decomp.).

On heating 1-*p*-toluidino*cyclo*pentane-1-carboxylic acid in a small distillation flask, water and *p*-toluidine, which was identified by converting it into its acetyl derivative, were evolved. The remainder distilled at a higher temperature, leaving no residue, and, on recrystallisation from petroleum, the *lactone* of 1-1'-*hydroxy*cyclo-*pentane*-1'-*carboxylyl*-p-*toluidino*cyclo*pentane*-1-*carboxylic acid* separated in colourless needles, m. p. 151° (Found : N, 4·7. $C_{19}H_{23}O_3N$ requires N, 4·5%). This lactone dissolves slowly in cold aqueous sodium hydroxide and is reprecipitated unchanged by the addition of dilute hydrochloric acid. It is not soluble in dilute acids and is unchanged by heating with aniline at 170° or dry ammonia at 200°.

3-*Methylcarbazole*.—An intimate mixture of 1-*p*-toluidino*cyclo*-pentane-1-carboxylic acid (16 g.), potassium hydroxide (36 g.), and sodium ethoxide (40 g.) was heated at 350° for 30 minutes. The product was pulverised and added to water, when 3-methylcarbazole separated. It was purified by distillation and subsequent recrystallisation from glacial acetic acid and obtained in colourless, glistening plates, m. p. 207° (compare Ullmann, *Ber.*, 1898, **31**, 1697). Its picrate separated from benzene in scarlet needles, m. p. 179° (compare Ullmann, *Annalen*, 1904, **332**, 88). The 3-methylcarbazole prepared in this way dissolved in concentrated sulphuric acid to give a pale green solution, which became intensely green on addition of a few drops of nitric acid.

3-Methylcarbazole was also synthesised very conveniently by boiling a solution of 6-methyltetrahydrocarbazole (3 g.; prepared from *p*-tolylhydrazine and *cyclo*hexanone; Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 62) and sulphur (1·05 g.) in pure quinoline (10 c.c.) for 25 minutes and then pouring it into dilute hydrochloric acid–ice. The 3-methylcarbazole which separated, after distillation with a small quantity of iron powder and recrystallisation of the distillate from glacial acetic acid, was obtained in colourless plates, m. p. 207°. Mixed with the product derived from 1-*p*-toluidino-*cyclo*pentane-1-carboxylic acid, it showed no depression of m. p., and its colour reactions with concentrated sulphuric acid and nitric acid were as above (compare Ullmann, *loc. cit.*). The picrate of this specimen of 3-methylcarbazole, crystallised from benzene, melted at 180°.

3 : 6-*Dimethyltetrahydrocarbazole*.—A mixture of 4-methyl*cyclo*-hexanone (5·5 g.), *p*-tolylhydrazine (6 g.), and alcohol (5 c.c.) was

gently warmed; on cooling, 4-*methyl*cyclo*hexanone*-p-*tolylhydrazone* separated. It was warmed to boiling with dilute sulphuric acid and heated on the steam-bath for an hour. The 3 : 6-*dimethyltetrahydrocarbazole* that separated crystallised from petroleum in small, colourless needles, m. p. 112° (Found: N, 7·0. $C_{14}H_{17}N$ requires N, 7·0%). Its *picrate* separated from benzene in dark red prisms, m. p. 147°.

3 : 6-*Dimethylcarbazole* was prepared from 3 : 6-dimethyltetrahydrocarbazole (3·2 g.) and sulphur (1 g.) in quinoline (5 c.c.) as described above. The oily product, which gradually solidified, was distilled with iron powder and thereafter crystallised from benzene, dimethylcarbazole being thus obtained in colourless needles, m. p. 219° (compare Täuber and Loewenherz, *Ber.*, 1891, **24**, 1033). 3 : 6-Dimethylcarbazole gives a faintly brown solution in concentrated sulphuric acid, the colour being intensified on addition of nitric acid. The picrate of 3 : 6-dimethylcarbazole separated from benzene in red needles, m. p. 192° (compare Täuber and Loewenherz, *loc. cit.*). A mixture of this 3 : 6-dimethylcarbazole with the 3-methylcarbazole obtained from 1-*p*-toluidino*cyclo*pentane-1-carboxylic acid melted completely below 197°.

One of us (S. G. P. P.) wishes gratefully to acknowledge the receipt of a grant from the Chemical Society Research Fund which has defrayed a part of the cost of this investigation.

THE DYSON PERRINS LABORATORY,
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CLVII.—*The Hydrolysis of Guanidine.*

By JAMES BELL.

WHILE it is generally accepted that urea is the product of the direct hydrolysis of guanidine in accordance with the simple equation

$$CN_3H_5 + H_2O = CON_2H_4 + NH_3 \quad . \quad . \quad . \quad (1)$$

the mechanism of this reaction has not hitherto been investigated. Ossikovszky (*Bull. Soc. chim.*, 1872, **18**, 161) obtained ammonia and carbon dioxide on boiling a solution of guanidine sulphate with excess of alkali and of acid, respectively: he therefore concluded that urea was formed as an intermediate product in this decomposition. The credit of being the first to obtain urea from guanidine is given to Baumann, whose only reference to this reaction consists of one sentence (*Ber.*, 1873, **6**, 1376), where he

states, without giving his experimental evidence, that urea can be obtained by boiling the solution of a guanidine salt with excess of barium hydroxide solution. Almost thirty years later, Fleming (*Chem.-Ztg.*, 1900, **24**, 56) obtained impure urea in this way, but gave no quantitative results. Krall, however, in an attempt to investigate the mechanism of this reaction, was unable to obtain any urea on boiling a solution of the free guanidine base under a reflux condenser (J., 1915, **107**, 1396).

By means of the xanthhydrol test (Fosse, *Compt. rend.*, 1913, **157**, 948) the author has been able to establish definitely the formation of urea, and to determine the extent of the reaction under various conditions. From the results obtained, information has been gained as to the mechanism of the reaction and of the accompanying secondary changes.

When a solution of free guanidine was boiled under a reflux condenser, ammonia gas was evolved and cyanate, carbonate, and urea were detected in the solution. In certain reactions, where urea, ammonium cyanate, and carbonate are produced, it has been shown that cyanic acid is first formed and is then hydrolysed on the one hand to ammonium carbonate, while on the other it combines in its *iso*-form with ammonia to form urea (Werner and Fearon, J., 1920, **117**, 1078). It has now been proved, however, that, in the case of guanidine, urea is the first product formed. When an aqueous solution of guanidine was allowed to remain at the ordinary temperature, the odour of ammonia developed and urea was found present, but no cyanate could be detected by the delicate copper–pyridine test (Werner, J., 1923, **123**, 2577). Barium nitrate also gave a negative test for carbonate, which was confirmed by the fact that the alkalinity of the solution remained constant. The first phase in the hydrolysis of guanidine is, therefore, represented by equation 1, the mechanism of which is discussed later.

It would thus appear that the production of ammonium cyanate and carbonate was due to the decomposition of urea, when boiled in the strongly alkaline solution of free guanidine (Werner, J., 1918, **113**, 84). This decomposition by guanidine was definitely proved by an experiment in which one equivalent of urea was added to a solution of guanidine, when an increase was obtained in the amount of cyanate and carbonate produced on boiling (Expt. 8). The next phases are therefore:

$$CON_2H_4 = NH_4OCN \quad . \quad . \quad . \quad . \quad (2)$$

$$NH_4OCN + 2H_2O = (NH_4)_2CO_3 \quad . \quad . \quad . \quad . \quad (3)$$

When a sufficiently dilute solution of guanidine was boiled under a reflux condenser, there was no escape of carbon dioxide, resulting

from the dissociation of ammonium carbonate, whereas the amount of ammonia evolved was greater than that required for equation 1. This could only arise from the further changes:

$$NH_4OCN + CN_3H_5 = CN_3H_5,HOCN + NH_3 \quad . \quad . \quad . \quad (4)$$
$$(NH_4)_2CO_3 + 2CN_3H_5 = (CN_3H_5)_2,H_2CO_3 + 2NH_3 \quad . \quad . \quad (5)$$

The amount of ammonia evolved was equal, within the limits of experimental error, to that required by these equations. It should be clearly understood that the latter changes (equations 4 and 5) took place under the special conditions stated above. With stronger solutions of guanidine, some carbon dioxide escaped through the reflux condenser and was not, therefore, all fixed as guanidine carbonate. Moreover, when a solution of guanidine was boiled without a reflux condenser, all the carbon dioxide escaped, urea and guanidine cyanate being left in the solution.

When investigating the rates of formation of these different products, it was noticed that, after a time, the proportion of guanidine cyanate present decreased as the reaction proceeded, showing that it also was undergoing change. Bamberger (*Ber.*, 1887, **20**, 68) has brought forward evidence for the isomeric change of guanidine cyanate to dicyanodiamidine in accordance with the equation

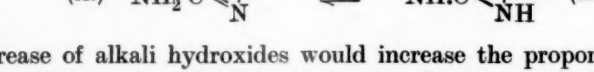
$$NH_2{\cdot}C(:NH){\cdot}NH_2,HOCN = NH_2{\cdot}C(:NH){\cdot}NH{\cdot}CO{\cdot}NH_2.$$

The latter compound, however, could not be detected in the products formed during the hydrolysis of guanidine, and is therefore not formed under the conditions in question. Even after evaporation of some of the neutralised solution to dryness, no change of guanidine cyanate to dicyanodiamidine occurred. There can be no doubt that guanidine cyanate forms only urea or guanidine carbonate, or, in all probability, both these substances, a conclusion which is also the only one consistent with the quantitative data. More definite information as to the hydrolysis of guanidine cyanate would require separate investigation.

On boiling dilute solutions of guanidine (of approximately $N/8$ strength), no evidence could be obtained of its dissociation into ammonia and cyanamide. However, when a normal solution was boiled, dissociation to a small extent was indicated by the formation of melamine, $C_3N_6H_6$, the tripolymeride of cyanamide. This dissociation is obviously a side reaction and not concerned in the formation of urea, since, in the first place, cyanamide does not produce urea under the conditions of these experiments, and in the second, a greater yield of melamine would have been obtained, in view of the ready polymerisation of cyanamide.

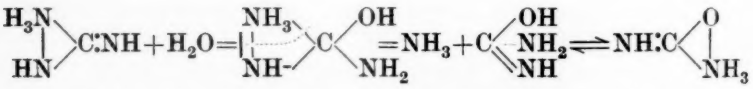
Krall (*loc. cit.*) has given reasons for doubting the usually accepted

formula for guanidine, *viz.*, $NH{:}C(NH_2)_2$, and suggests that in solution, the free base exists probably as an equilibrium mixture of the two forms



(A.) (B.)

Increase of alkali hydroxides would increase the proportion of B, and addition of acids that of A. In the course of the present work, additional evidence has been obtained in favour of this view. When a solution of free guanidine in presence of excess of alkali was kept at the laboratory temperature, the rate of formation of urea was greater than in the case of guanidine alone, whilst the alkali appeared to take no part in the reaction (Expts. 1 and 2). This fact is explained most easily on the above conception of the constitution of guanidine. As a rule, the NH: radical is the more readily hydrolysed, and hydrolysis would therefore take place through the B form. The presence of additional alkali increases the proportion of B and therefore increases also the rate of hydrolysis. The mechanism of the reaction may be best explained thus:



This view of the constitution of guanidine has received support from Plimmer in his recent investigation of its behaviour towards nitrous acid (J., 1925, **127**, 2658).

Experimental.

A solution of free guanidine was prepared by the precipitation of guanidine carbonate solution with one equivalent of barium hydroxide solution and filtering off the barium carbonate. The filtrate, which was an approximately *N*/8-solution, always contained some guanidine carbonate, owing to the absorption of carbon dioxide from the air by the strongly alkaline liquid during filtration. This carbonate was estimated at the outset and the necessary corrections were applied throughout.

In the experiments described, the urea formed was estimated by neutralising an aliquot part of the liquid, evaporating the solution to dryness, extracting the residue with glacial acetic acid, and adding excess of xanthhydrol, dissolved in methyl alcohol. After 12 hours, the precipitate of dixanthylurea was collected on a weighed filter-paper, washed with alcohol, dried, and weighed. A small correction was applied for the slight solubility of dixanthylurea in the mixture of acetic acid and methyl alcohol, the value of this

correction being determined in preliminary control experiments. The carbon dioxide in solution was estimated volumetrically, after precipitation as barium carbonate. Cyanates were estimated by precipitation and weighing as silver cyanate.

Dicyanodiamidine was tested for by adding copper sulphate and sodium hydroxide solutions, when the characteristic pink copper derivative of this substance was precipitated. Melamine was identified by its picrate.

In all the experiments, where a solution of guanidine was boiled, the burner was adjusted to secure quiet ebullition only.

Expt. 1. Changes produced in $N/8$-solution of guanidine at the ordinary temperature. *a* is the percentage of guanidine hydrolysed to urea.

Time (days) ...	5	10	20	31	60	70	156	189
a	3·25	6·1	11·3	19·2	31·4	35·1	62·4	70·5

No cyanate or carbonate was formed.

Expt. 2. Changes produced at the ordinary temperature in $N/8$-solution of guanidine containing sodium hydroxide (1 mol.).

Time (days)	8	41	102	128
a	9·5	34·5	64·9	70·4

Here the velocity of hydrolysis was greater than in the solution of guanidine alone. No cyanate or carbonate could be detected.

Expt. 3. Changes produced in $N/8$-solution of guanidine after $1\frac{1}{2}$ hours' boiling under reflux.

100 C.c. of solution were used containing 0·702 g. of the free base. Urea, cyanate, and carbonate in the resulting liquid were estimated. Increase in alkalinity of liquid on boiling = 9·8 c.c. of $N/10$-acid (this included the ammonia evolved). This increase could only be due to the formation of ammonium carbonate as in equation 3. Increase in alkalinity, calculated from the carbonate found in solution, = 9·9 c.c. of $N/10$-acid. Hence no carbon dioxide escaped through the condenser. The ammonia evolved, calculated from equations 1, 4, and 5, = 8·05 c.c. of N-acid (Found: NH_3 = 8·0 c.c. of N-acid). The following results represent the percentages of the different products, calculated in terms of the guanidine, from which each was originally derived, in accordance with equations 1—5: Urea, 36·5; ammonium cyanate, 9·05; ammonium carbonate, 4·15; guanidine cyanate, 9·07; guanidine carbonate, 8·30. Total, 67·05%.

Expt. 4. Changes produced in $N/8$-solution of guanidine after boiling under reflux for 3 hours.

Increase in alkalinity, calculated from the carbonate present, = 13·0 c.c. of $N/10$-acid. Increase found = 13·0 c.c. of $N/10$-acid.

Ammonia evolved = 4·45 c.c. of *N*-acid. Calc.: NH_3 = 11·25 c.c. of *N*-acid. This was the only experiment in which the ammonia was not all driven out of solution. Found: Urea, 66·0; ammonium cyanate, 6·25; ammonium carbonate, 7·05; guanidine cyanate, 6·25; guanidine carbonate, 14·10. Total, 99·65%.

Expt. 5. Changes produced in *N*-solution of guanidine after 1½ hours' boiling under reflux.

A normal solution of guanidine was prepared by dissolving 4·13 g. of guanidine nitrate in 33·8 c.c. of *N*-sodium hydroxide solution. After boiling, urea, carbonate and cyanate were estimated as before. Increase in alkalinity = 6·4 c.c. of *N*-acid. Increase due to the carbonate found in solution = 3·0 c.c. of *N*-acid. Hence, ammonium carbonate formed = 6·4 c.c. of *N*-acid, and of this, a portion = 3·4 c.c. of *N*-acid, passed through the condenser, whilst the remainder = 3·0 c.c. of *N*-acid, reacted with free guanidine to form guanidine carbonate. Found: Urea, 59·5; ammonium cyanate, 6·45; ammonium carbonate, 9·4; guanidine cyanate, 6·45; guanidine carbonate, 8·9. Total, 90·7%.

Found for the ammonia evolved, 35·2 c.c. of *N*-acid. Calc., 34·2 c.c. The difference is due to ammonia involved in the formation of melamine, a small quantity of which was present. This difference would correspond to a 3% conversion into melamine.

Expt. 6. Changes produced in *N*/15-solution of guanidine containing one equivalent of barium hydroxide, after 1½ hours' boiling under reflux.

The results, in this case, were similar to those of the previous experiments, except that barium cyanate and carbonate were produced instead of the corresponding guanidine salts. The ammonia evolved was not estimated. Found: Urea, 80·0; barium cyanate, 13·4; barium carbonate, 2·9. Total, 96·3%.

Expt. 7. Changes produced in *N*/7-solution of guanidine, after 1 hour's boiling without reflux.

The solution was boiled in a distillation flask, connected with a condenser and flask for ammonia absorption. Water was added from a tap funnel at intervals to maintain the volume of the solution constant. No carbonate was found in the solution on boiling. Hence all the carbon dioxide escaped. The amount of ammonium carbonate formed was calculated from the increase in alkalinity.

Found for ammonia evolved, 14·3 c.c. of *N*-acid. Calc., 14·4 c.c. Found: Urea, 73·4; ammonium carbonate, 1·4; ammonium cyanate, 9·6; guanidine cyanate, 9·6%. Total, 94·0%.

Expt. 8. Action of guanidine on urea in solution on boiling.

A solution similar to that used in the previous experiment, containing one equivalent of urea (0·9 g.), was boiled for 1 hour under

the same conditions. It was assumed that the changes produced in the guanidine were the same as before. The increase in carbonate and cyanate was therefore due to the decomposition of the added urea. Found: Added urea converted into ammonium cyanate and carbonate = 13·3 and 3·7%, respectively. Therefore total urea decomposed = 17·0%.

From the determination of urea in the two experiments, the decomposition of added urea was calculated to be 21·9%. The difference in these results is due to the fact that, in this experiment, more guanidine was fixed as cyanate than in the previous one, and hence the amount of guanidine hydrolysed would be slightly less.

The author gratefully acknowledges his indebtedness to Professor E. A. Werner, Sc.D., for advice received in the course of this work and to Dr. W. R. Fearon, F.T.C.D., at whose suggestion this investigation was undertaken.

TRINITY COLLEGE, DUBLIN. [*Received, February 16th*, 1926.]

CLVIII.—*Nitrosylsulphuric Acid. Part I.*

By GEORGE ALBERT ELLIOTT, LESLIE LEONARD KLEIST, FREDERICK JAMES WILKINS, and HARRY WILLIAM WEBB.

THE object of this investigation was to examine the constitution and properties of nitrosylsulphuric acid.

To the substance of the molecular formula HSO_5N have been ascribed two structural formulæ, *viz.*, that of nitrosulphonic acid (I) (Michaelis, *Ber.*, 1874, **7**, 1075; Raschig, *Z. angew. Chem.*, 1905, **18**, 1032) and that of nitrosylsulphuric acid (II) (Tilden, J., 1874, **27**, 630; Lunge, *Ber.*, 1879, **12**, 1058). The evidence for the existence of an acid of the structure (I) is unsatisfactory.

(I.) $O_2S\begin{<}NO_2\\OH\end{}$ $\qquad$ $O_2S\begin{<}O{\cdot}NO\\OH\end{}$ (II.)

We first prepared the acid by several different methods and found that its melting point and crystalline form did not vary with the method used. Fractional crystallisation from sulphuric acid also failed to effect any change. Therefore, whilst the acid may be tautomeric, the existence of non-dynamic isomerides is improbable.

The action of hydrogen chloride on the crystalline acid at the ordinary temperature rapidly led to the formation of nitrosyl chloride and sulphuric acid, the reaction being reversible, as was

foreshadowed by the work of Tilden (*loc. cit.*). The presence of the nitroso-group thus indicated was more definitely suggested by the reaction between the acid and benzoyl chloride, which produced *dibenzoylsulphuric acid*, $O_2S(O{\cdot}CO{\cdot}C_6H_5)_2$, whose formation can be satisfactorily explained only on the assumption that nitrosylsulphuric acid contains both a nitroso- and a hydroxyl-group. The mechanism of the reaction would then be as follows. The first stage is the formation of *monobenzoylsulphuric acid* :

$$OH{\cdot}SO_2{\cdot}O{\cdot}NO + PhCOCl = OH{\cdot}SO_2{\cdot}O{\cdot}COPh + NOCl.$$

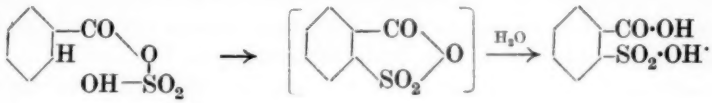
Nitrosyl chloride is actually formed as soon as the two substances are mixed and is rapidly liberated at 35—40° without appreciable heat evolution. The monobenzoylsulphuric acid then reacts additively with a further molecule of benzoyl chloride, probably at the carbonyl group of the latter, and a crystalline product is obtained which loses hydrogen chloride on standing, dibenzoylsulphuric acid being formed :

$$PhCOCl + OH{\cdot}SO_2{\cdot}O{\cdot}COPh = PhCCl(OH){\cdot}O{\cdot}SO_2{\cdot}O{\cdot}COPh.$$

Confirmation of this mechanism was obtained by examining the reaction between benzoyl chloride and sulphuric acid. Oppenheim (*Ber.*, 1870, **3**, 736) states that this reaction yields a benzoylsulphuric acid which rapidly changes to *m*-sulphobenzoic acid on standing, and that the latter is formed exclusively if the reaction is carried out at 150°. No mention of an additive product is made and the experimental data are very meagre. We have found that the substance produced at the ordinary temperature is a crystalline additive compound, to which the constitution $PhCCl(OH){\cdot}O{\cdot}SO_2{\cdot}OH$ may most readily be assigned. It loses hydrogen chloride on standing, forming monobenzoylsulphuric acid; this change, however, is inhibited by an atmosphere of hydrogen chloride. The additive compound showed no sign of transformation into sulphobenzoic acid on being kept for 6 months over a dry alkaline absorbent at the ordinary temperature, although during this time the hydrogen chloride was completely eliminated.

At 100°, the highest temperature used in our experiments, conversion of benzoylsulphuric acid into sulphobenzoic acid occurred, but so slowly that the amount formed during our experiments could be neglected in making deductions from the results obtained. The change was a unimolecular one and the product consisted mainly of *o*- and not *m*-sulphobenzoic acid. It is probable that the meta-acid, stated by Oppenheim to be the sole product, is produced by direct sulphonation, and the ortho-acid by intramolecular transformation. The production of the ortho-acid in this way can

be satisfactorily explained by assuming intermediate anhydride formation and subsequent rehydration :



We were unable to obtain pure dibenzoylsulphuric acid by the interaction of benzoyl chloride and sulphuric acid.

The action of acetyl chloride on nitrosylsulphuric acid yielded similar evidence of the presence of the nitroso-group. The first product of the reaction appears to be acetylsulphuric acid, but this changes with great rapidity into the isomeric sulphoacetic acid. The evidence for this change lies in the rapid decrease in the amount of free sulphuric acid produced by the decomposition of the product with water, whilst the total sulphur content of the substance remains constant. The change is very much more rapid than that of benzoylsulphuric acid, but we did not investigate it further as it had already been examined by Van Peski (*Rec. trav. chim.*, 1921, **40**, 103) and others.

The action of acetic anhydride on nitrosylsulphuric acid also yielded acetylsulphuric acid. Equimolecular quantities of the two substances without any diluent reacted so violently at the ordinary temperature that the sudden evolution of heat was usually sufficient to shatter the glass container. If the acetic anhydride was in great excess and was kept below 15° during the addition of the nitrosylsulphuric acid, the latter dissolved, and by shaking the solution with silver oxide a substance was obtained to which the constitution $CH_3{\cdot}CO{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}NO,CH_3{\cdot}CO_2Ag$ is assigned.

By the action of ether on nitrosylsulphuric acid, ethyl nitrite and ethyl hydrogen sulphate were produced :

$$HO{\cdot}SO_2{\cdot}O{\cdot}NO + (C_2H_5)_2O = C_2H_5{\cdot}HSO_4 + C_2H_5{\cdot}O{\cdot}NO.$$

Ethyl hydrogen sulphate and solutions of nitrosylsulphuric acid in sulphuric acid gave no nitroethane, which one would expect to be produced if the acid had the nitrosulphonic structure.

The most important evidence for the nitrosulphonic structure and possible tautomerism of the acid is the work of Biehringer and Borsum (*Ber.*, 1916, **49**, 1402). By treating a sulphuric acid solution of dimethylaniline with solid sodium nitrite they obtained mixtures of *p*-nitro- and *p*-nitroso-dimethylaniline. We decided to repeat their work, for three reasons : (1) The setting up of equilibria involving the two forms of nitrous acid and sulphuric acid was not excluded by their method of experiment. (2) Since

they poured a reaction mixture containing an excess of nitrite on ice, direct nitration of unchanged dimethylaniline and secondary oxidation of the nitroso-derivative would be expected. (3) They do not mention the production of sulphur dioxide which would be expected as a by-product from the nitrosulphonic form.

Using a solution of crystalline nitrosylsulphuric acid in sulphuric acid, of concentration equivalent to that used by them, we confirmed the result that both *p*-nitro- and *p*-nitroso-dimethylaniline are produced. We also established the following facts : (1) The percentage yield of the *p*-nitro-derivative increases with the excess of nitrosylsulphuric acid used in the reaction mixture. (2) If an excess of dimethylaniline is used, no oxides of nitrogen are produced by pouring the mixture on ice and no *p*-nitro-derivative is obtained. (3) When an excess of nitrosylsulphuric acid is present and the mixture is poured into absolute alcohol or dry ether, no *p*-nitro-derivative is obtained. Both these solvents rapidly decompose nitrosylsulphuric acid, forming ethyl nitrite and ethyl hydrogen sulphate. (4) When crystalline nitrosylsulphuric acid is added to a solution of dimethylaniline in dilute sulphuric acid (2*N*), in which the former acid is immediately decomposed, both the *p*-nitro- and the *p*-nitroso-derivative are obtained. (5) If a solution of dimethylaniline in concentrated sulphuric acid is added to a dilute solution of nitric acid (10%) or of potassium nitrite (5%), the *p*-nitro-derivative is formed. (6) No sulphur dioxide could be detected in any of the experiments.

All these facts are in accord with the view that the *p*-nitrodimethylaniline is not produced by the action of a presumed nitrosulphonic acid, but is a secondary product obtained by pouring the reaction mixture on ice and is produced either by secondary oxidation of the nitroso-compound or by direct nitration of the dimethylaniline. The results of Biehringer and Borsum do not establish, therefore, in our opinion, the existence of nitrosulphonic acid or the possibility of tautomerism.

Conversion of Nitrosylsulphuric Acid into the Anhydride.

The anhydride of nitrosylsulphuric acid is assumed to have the structure $ON{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}NO$ and is stated to be formed by the action of nitric oxide on sulphur trioxide, or of sulphur dioxide on well-cooled nitrogen pentoxide (Berl, *Z. angew. Chem.*, 1910, **23**, 2250).

There appears to be no definite experimental evidence for the direct conversion of nitrosylsulphuric acid into the anhydride, a change which would yield important evidence as to structure. We have examined the change by three methods :

(1) By the action of heat alone.

(2) By heating in the presence of dehydrating agents.

(3) By the determination of the solubility of the acid in sulphuric acid.

Action of Heat on Nitrosylsulphuric Acid.—Michaelis and Schumann (*Ber.*, 1874, **7**, 1075) carried out a preliminary investigation on this point and suggested that the decomposition took place according to the scheme :

$$NO_2\cdot SO_2\cdot OH + HO\cdot SO_2\cdot NO_2 \rightleftharpoons NO_2\cdot SO_2\cdot O\cdot SO_2\cdot NO_2 + H_2O.$$

Their experimental methods, however, were very rough, and no experimental evidence was offered that the final product was the anhydride. They ascribe the nitrosulphonic structure to the acid, but it is improbable that an acid of either the nitro- or the nitroso-structure would undergo a decomposition of the type suggested, in view of the great instability of these groups in the molecule.

Theoretically there is another mode of decomposition :

$$ON\cdot O\cdot SO_2\cdot OH + ON\cdot O\cdot SO_2\cdot OH \rightleftharpoons ON\cdot O\cdot SO_2\cdot O\cdot SO_2\cdot OH + HNO_2.$$

The nitrous acid would then decompose to form nitrogen trioxide and water, which would decompose more nitrosylsulphuric acid. The net result is represented by the equation $3HSO_5N = HS_2O_8N + H_2SO_4 + N_2O_3$. When decomposition is complete, the resulting liquid should yield 15·4% of nitrous acid by decomposition with water. If the reaction proceeds according to the suggestion of Michaelis, however, the percentage of nitrous acid so obtained should be 21·8. (By " percentage of nitrous acid " should be understood the amount of nitrous acid obtained by the complete decomposition of the residue with water, calculated as a percentage of the anhydrous substance.)

By following the change in the nitrous acid content we found that the decomposition by heat appears to follow the course suggested by Michaelis.

The Action of Dehydrating Agents.—The results obtained by heating the acid in the presence of dehydrating agents (phosphorus pentoxide in particular) were unsatisfactory. We were unable to detect the anhydride in the distillate : nitrosylsulphuric acid, the main product obtained, was probably formed by the recombination of sulphur trioxide, water, and nitrogen peroxide in the receiver. Dehydration of nitrosylsulphuric acid was also attempted by making a saturated solution in 98% sulphuric acid at 50°. The solution, after being heated for several hours at 100°, was cooled to 16° and found to be supersaturated. A crystal of nitrosylsulphuric acid induced crystallisation, the product being the un-

changed acid. Further experiments showed that nitrosylsulphuric acid appears to be capable of existence in saturated solution in sulphuric acid even at 300°. This is remarkable in view of the ease with which water is lost on heating the acid alone.

The Solubility of Nitrosylsulphuric Acid in Sulphuric Acid.— The method previously described for the attempted isolation of the anhydride would yield positive results only if the anhydride (if formed) were relatively less soluble in sulphuric acid than nitrosylsulphuric acid. We therefore examined the solubility of nitrosylsulphuric acid at 0°, 20·9°, 37·3°, and 49·6° in various concentrations of sulphuric acid. The curves expressing the relationship between the solubility of nitrosylsulphuric acid and the concentration of sulphuric acid all showed a marked increase in the solubility coefficient when the concentration of sulphuric acid reached 73%. Schlesinger and Salathe (*J. Amer. Chem. Soc.*, 1923, **45**, 1863) have investigated the absorption spectra of a series of 0·1*N*-solutions of nitrosylsulphuric acid in sulphuric acid of different concentrations. If the concentration of sulphuric acid is plotted against the frequency for a given value of the logarithm of the thickness in their results, the curves so obtained are similar to ours and show a change of slope at a concentration of 78% H_2SO_4.

The shape of our curves is not incompatible with the conclusion that anhydride formation takes place.

From some points of view, an alternative structure $O_2S\langle^{O}_{O}\rangle N\cdot OH$ seems to merit consideration. (1) An acid of this type would lose water on heating to give an anhydride of the structure (III), a change which is parallel to the conversion of nitric acid into nitrogen pentoxide. (2) It offers an explanation of the great difficulty of replacing both the hydroxyl groups of sulphuric acid by the nitroso-group. (3) The structure is in accord with the methods of synthesis of the acid. (4) The behaviour of the acid on reduction is more in accord with this structure than with the nitroso-structure. (5) The synthesis of the anhydride from sulphur dioxide and nitrogen pentoxide (Berl, *loc. cit.*) is readily explicable in terms of the above formula :

$$SO_2 + {}^{O}_{O}\!\gg\! N\cdot O\cdot N\!\ll\!{}^{O}_{O} + SO_2 = O_2S\langle^{O}_{O}\rangle N\cdot O\cdot N\langle^{O}_{O}\rangle SO_2 \quad \text{(III.)}$$

and so is the production of the anhydride from nitrogen tetroxide and sulphur dioxide (Provostaye, *Ann. Chim. Phys.*, 1840, **73**, 362), in which reaction nitrogen trioxide is a by-product :

$$SO_2 + {}^{O}_{O}\!\gg\! N\cdot O\cdot N{:}O + O{:}N\cdot O\cdot N\!\ll\!{}^{O}_{O} + SO_2 = \text{(III)} + N_2O_3.$$

It is possible that nitrosylsulphuric acid exists in two tautomeric forms, $O_2S<^{O\cdot NO}_{OH} \rightleftharpoons O_2S<^{O}_{O}>N\cdot OH$, which are in equilibrium in sulphuric acid solution and in the molten state.

EXPERIMENTAL.

Preparation of Nitrosylsulphuric Acid.—(1) By the addition of dry liquid nitrogen tetroxide to concentrated sulphuric acid at 15—18°. The separation of crystals and the removal of excess of tetroxide were facilitated by blowing dry air through the mass. (2) As above, but using gaseous nitrogen tetroxide. (3) By passing sulphur dioxide, dried by sulphuric acid, into pure nitric acid (94·5% HNO_3) at 25°. (4) By leading nitrosyl chloride, generated by heating aqua regia, into concentrated sulphuric acid.

The crystals in each case were rapidly drained by a pump and dried on a porous plate over sulphuric acid. All the products consisted of rhombic prisms (m. p. 73·5°). Tilden (*loc. cit.*) obtained by the last method of preparation a product of m. p. 85—87°, but we have not been able to repeat his work.

The Action of Benzoyl Chloride.—A mixture of 1 g.-mol. of nitrosylsulphuric acid with 2·4 g.-mols. of benzoyl chloride was heated for 30 minutes on the water-bath, moisture being excluded. After 12 hours, yellowish-brown, rhombic crystals separated. These were filtered off rapidly on asbestos, washed with dry carbon tetrachloride, and dried on a porous plate over phosphorus pentoxide. The product was very hygroscopic. It had no odour of benzoyl chloride, and on treatment with water it was completely decomposed into sulphuric, benzoic, and hydrochloric acids. Ethyl alcohol was readily converted by it into ethyl benzoate. It was insoluble in all common organic solvents and reacted readily with substances containing a hydroxyl group and with ether and acetone. No evidence of the presence of an acid with a sulphonic group could be obtained. The product was analysed as follows: A weighed sample was warmed with excess of water until completely dissolved. The total acidity was then determined by sodium hydroxide and phenolphthalein, and the sulphuric acid as barium sulphate. Hydrochloric acid was estimated by silver nitrate and ammonium thiocyanate. As an approximate check on the results the benzoic acid was estimated in several samples by removing the sulphuric acid with baryta, slightly acidifying the solution with hydrochloric acid, extracting with ether, and weighing the dried product. The hydrochloric acid content of the samples varied with the time which elapsed before analysis and, in order to make apparent the composition of the acidic residue, the analyses are

expressed in terms of hydrochloric acid-free substance. For convenience of expression also, the acidities obtained after aqueous decomposition are expressed as percentages of the anhydrous substance. The same device is used also for the theoretical values, which are those calculated for $(PhCO{\cdot}O)_2SO_2,HCl$.

				Calc. for HCl-free product.			
Sample.	% Total acidity, as H_2SO_4.	% H_2SO_4.	% HCl.	% Total acidity, as H_2SO_4.	% H_2SO_4.	% $PhCO_2H$.	Remarks.
1	71·55	28·66	10·60	64·18	32·06	—	Dried in an atmosphere of HCl.
2	66·00	31·01	3·00	63·89	31·97	—	Analysed after 3 weeks.
3	69·01	29·75	7·30	63·89	32·09	76·73	Analysed after 24 hours.
Theory	71·53	28·61	10·66	64·05	32·02	79·73	

The hydrochloric acid content does not exceed one molecule, and sample 1, dried in hydrochloric acid vapour, approximates closely to the theoretical value. It might be expected that a substance of the nitrosulphonic structure under the conditions of our experiments would yield sulphur dioxide as a decomposition product. 2·4 G.-mols. of benzoyl chloride were heated on the water-bath with 1 g.-mol. of nitrosylsulphuric acid, and the evolved gases drawn through potassium dichromate solution. The amount of sulphur thus found as sulphur dioxide is shown as a percentage of the total sulphur.

Time (hours)	2	4	6	8	10	12
% S as SO_2	0·49	0·44	0·26	0·19	0·10	0·02

The results indicate that about 1·5% of the total sulphur is evolved as sulphur dioxide on continued heating at 100°. Although the rate of evolution decreases with time, it is considered that the sulphur dioxide is formed by reduction of sulphuric acid and is not due to the presence of the nitrosulphonic form of the acid, since benzoyl chloride and sulphuric acid yield a similar result (*q.v.*).

Action of Sulphuric Acid on Benzoyl Chloride.—The first method used was to mix benzoyl chloride (1 or 2 mols.) with concentrated sulphuric acid. The manner of mixing made a great difference to the purity of the product and to the hydrogen chloride content. If the sulphuric acid was added to the benzoyl chloride, the solution became deep green and most of the chlorine was evolved as hydrogen chloride. If the reverse process was adopted, the coloration was much less and the evolution of hydrogen chloride was very small at the ordinary temperature. Preparations were made in this way,

using sulphuric acid varying in concentration from 96 to 100% at temperatures from 0—40°. The products were treated and analysed as previously described for nitrosylsulphuric acid.

Mode of addition.		Temp.	% Total acidity, as H_2SO_4.	% H_2SO_4.	% HCl.
2 g.-mol. PhCOCl to 1 g.-mol. H_2SO_4.	(1)	30°	76·50	37·55	12·75
	(1A) *	17	67·52	38·29	3·64
	(2)	32	70·11	35·80	10·13
	(3)	30	69·80	36·50	12·91
1 g.-mol. H_2SO_4 to 2 g.-mols. PhCOCl.	(1)	29	77·66	35·65	14·27
	(2)	30	77·87	35·32	14·47
	(3) †	28	73·30	34·54	9·85
	(4)	0	80·21	38·27	15·30
	(5)	0	79·41	37·43	15·16
	(6)	0	80·63	38·77	14·70
1 g.-mol. H_2SO_4 to 1 g.-mol. PhCOCl.	(1)	0	77·30	43·90	8·19
	(2)	0	76·40	45·08	7·01
Theory for $PhCO{\cdot}O{\cdot}SO_2{\cdot}OH,HCl$			82·18	41·09	15·34

* After 48 hours over lime. † After keeping 48 hours.

The last two preparations, when calculated to hydrochloric acid-free product, gave total acidity = 72·24, 72·06% H_2SO_4, and sulphuric acid = 47·82, 48·48%, respectively, whereas the values theoretically required are 72·77 and 48·51%.

The repetition of the exact experimental conditions used in the case of nitrosylsulphuric acid yielded products which appeared to be mixtures of mono- and di-benzoylsulphuric acids or of the mono-acid and sulphobenzoic acid. Preparations carried out at 16° and 30° gave similar products. At 0°, however, the products were very near in composition to the mono-acid.

In view of the difficulty of purifying the products, the method of preparation was further improved by dissolving the benzoyl chloride in excess of dry carbon tetrachloride, adding the 98% sulphuric acid gradually with continuous shaking, and keeping the mixture for 30 minutes, with exclusion of moisture. In this way, it is immaterial whether 1, 2, or 3 molecular proportions of benzoyl chloride are used and the temperature can also be varied between 0—35° without affecting the purity of the product: the yield is theoretical. Analyses of typical products were as follows:

	% Total acidity as H_2SO_4.	% H_2SO_4.	% HCl.
1	78·40	44·02	9·20
2	78·88	43·64	10·00
3	78·78	43·31	10·04

The total sulphur content of the products was determined by fusion, and the fact that the figure so obtained was identical with that for the percentage of sulphuric acid obtained by decomposing the substance with water was taken to indicate the absence of

sulphobenzoic acid from the products. This estimation was carried out as follows. To 1 g. of the substance contained in a platinum dish about 5 g. of moistened sodium peroxide were added and the mixture was stirred with a platinum rod. The product was intimately mixed with 30—40 g. of a mixture of 1 part of potassium nitrate and 2 parts of fusion mixture. The top of the mass was then covered with 15—20 g. of fusion mixture, and the whole heated gently until fusion was complete. If signs of charring appeared, the determination was repeated. The method was much quicker than a Carius estimation and better than the Eshka method for the substances under analysis. The method is given in detail, as duplicates showed it to be quite satisfactory.

Transformation of Benzoylsulphuric Acid into Sulphobenzoic Acid.—Determinations were made of the total sulphur content of a number of products by fusion, and of the sulphuric acid produced by decomposition with water. The samples were prepared using equimolecular proportions of sulphuric acid and benzoyl chloride at 0°, 16°, and 120°. The results were as follows :

	1.	2.	3.
Sulphuric acid by water treatment (H_2SO_4 %)	42·31	43·30	37·40
Total sulphur (by fusion) as H_2SO_4 %	42·16	43·16	37·43

This evidence for the absence of sulphobenzoic acid is conclusive unless the latter is completely decomposed by treatment with warm water. No satisfactory information could be found in the literature on this point and therefore we determined the velocity of transformation of benzoylsulphuric acid into sulphobenzoic acid at 100°, the highest temperature used in our experiments. 70 G. of monobenzoylsulphuric acid were heated, in a constant-temperature bath at 100°, in a flask fitted with a moisture trap. The gases were drawn off continuously through potassium dichromate and the sulphur dioxide content was estimated. Samples of the residue in the flask were drawn off at intervals and the sulphuric acid produced by decomposition with water was estimated. At the conclusion of the heating the total sulphur content of the residue was determined by the fusion method previously described.

Time (hours).	% H_2SO_4 obtained.	k.	% Total S lost as SO_2.
0	43·20	—	—
10	36·67	0·01639	0·26
15	33·83	0·01630	0·25
20	31·14	0·01637	0·23
25	28·75	0·01628	0·22

Total sulphur content of the residue after 25 hours = 42·10% as H_2SO_4. k is calculated on the basis of a unimolecular reaction.

Isolation of Sulphobenzoic Acid [With R. PEPPERELL].—The above

material which had been heated for 25 hours at 100° was warmed with 500 c.c of water and concentrated to 250 c.c. The precipitated benzoic acid was filtered off and the sulphuric acid precipitated with baryta and filtered off. This filtrate was concentrated to 100 c.c., and the excess of barium exactly precipitated with sulphuric acid. The barium sulphate and any further benzoic acid were removed and the filtrate was evaporated to small bulk and extracted with ether until no further benzoic acid could be obtained. The residue on final concentration on the water-bath solidified to an amorphous hygroscopic mass which was dried by heating to 105° (Found : S, 16·1. Theory for $CO_2H{\cdot}C_6H_4{\cdot}SO_3H$: S, 15·8%). The substance did not melt sharply, but was completely molten at 135°. The anhydride (m. p. 129—130°) was prepared by refluxing with acetyl chloride for 2 hours and extraction with benzene. The acid also condensed readily with resorcinol in presence of zinc chloride to give a phthalein. The product was hence *o*-sulphobenzoic acid, but the original substance contained some meta-acid also.

Action of Acetyl Chloride.—25 G. of nitrosylsulphuric acid were added slowly to 35 g. of acetyl chloride dissolved in 100 c.c. of carbon tetrachloride, and the mixture was warmed to 30—35° to start the reaction. A vigorous evolution of nitrosyl chloride occurred, the temperature rising to 60—70°, and a yellow, viscous, non-crystallisable oil separated. This was washed repeatedly with carbon tetrachloride and ligroin and analysed as rapidly as possible by methods similar to those used in the case of the corresponding benzoyl derivative (Total acidity, as H_2SO_4, 101·9; H_2SO_4, 68·4. $CH_3{\cdot}CO{\cdot}O{\cdot}SO_3H$ requires 105·0 and 70·0%, respectively). The substance was completely decomposed by water into acetic and sulphuric acids.

The product was heated under reflux in carbon tetrachloride for 30 minutes and the percentage of sulphuric acid obtained by decomposition with water was reduced to 54·32% from 68·40%. After another hour's refluxing, it was further reduced to 27·58%, the total sulphur content remaining constant.

Action of Acetic Anhydride.—(1) 10 G. of acetic anhydride were dissolved in 200 c.c. of carbon tetrachloride and 12 g. of nitrosylsulphuric acid were added. On refluxing for 30 minutes a yellow oil separated, from which the last traces of solvent were removed in a vacuum. (2) 5 G. of nitrosylsulphuric acid were dissolved in 200 c.c. of acetic anhydride, the mixture being kept cool, and the solution was shaken with 5 g. of dry silver oxide. The silver oxide was rapidly converted into a gelatinous suspension, which was filtered off in a vacuum, washed with acetic anhydride, and dried over sulphuric acid. The product was amorphous and

hygroscopic and on treatment with water gave no oxides of nitrogen. The resulting solution gave no precipitate with barium nitrate. Liebermann's reaction showed the presence of nitrite or a nitroso-group in the substance. The salt contained sulphur, nitrogen, and silver, in addition to carbon, hydrogen, and oxygen (Ag, by heating, 31·5; by conversion to AgCl, 32·0. S, estimated as $BaSO_4$, 9·4. $CH_3{\cdot}CO{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}NO,CH_3{\cdot}CO_2Ag$ requires Ag, 32·1; S, 9·5%).

Action of Nitrosylsulphuric Acid on Dimethylaniline.—(1) To a solution of 35 g. of dimethylaniline in 40 c.c. of concentrated sulphuric acid a solution of 70 g. of nitrosylsulphuric acid in 30 c.c. of sulphuric acid was added, at 10—15°. By following the experimental procedure of Biehringer and Borsum (*loc. cit.*) there were obtained : *p*-nitrodimethylaniline, 63%; *p*-nitrosodimethylaniline, 37%. (2) The above experiment was repeated using half the amount of nitrosylsulphuric acid (*i.e.*, an excess of dimethylaniline). No nitro-derivative was obtained but only the nitroso-derivative. (3) Quantities as in Expt. (1) were used and the mixture was dropped slowly into absolute alcohol at 0°. No nitro-derivative was obtained. By pouring the product into 300 c.c. of dry ether a mixture of the sulphates of dimethylaniline and *p*-nitrosodimethylaniline was obtained. Some nitric oxide was evolved on first mixing the reactants, but no sulphur dioxide could be detected at any stage of the reaction.

Action of Heat on Nitrosylsulphuric Acid.—(1) 30 G. of the crystalline acid were heated for 30 minutes at 350° in a wide glass tube fitted with a moisture trap; nitrogen trioxide was rapidly evolved during the first 15 minutes. A pale yellow, very viscous oil remained (Found : HNO_2, 19·3%).

(2) 50 G. of nitrosylsulphuric acid were heated under similar conditions at 300° for 9 hours. The residual oil was analysed as before (Found : HNO_2, 20·2%).

At both these temperatures sulphur trioxide was evolved owing to the decomposition of the product, and this fact may explain the poor agreement with the value required by the suggestion of Michaelis. On attempting to carry out the decomposition at temperatures low enough to ensure that no sulphur trioxide was produced, it was found that the rate of decomposition was so slow that several weeks would be required for complete decomposition.

(3) 50 G. of the acid were heated in a constant-temperature bath at 150°. Samples were withdrawn at intervals and analysed as before.

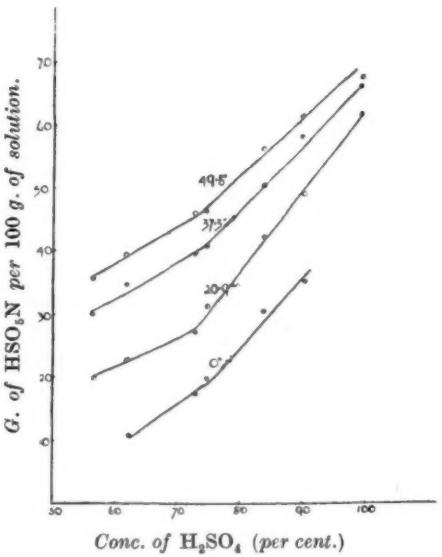
Time (hrs.) ...	0	0·75	11·3	16·5	26·3	39·0	46·8	59·3	137·0
% HNO_2.....	35·9	32·8	30·7	30·2	29·7	29·0	28·1	27·5	25·8

(Theoretical value for anhydride, 21·8% HNO_2.)

Similar determinations were carried out at 115° and 130° and in each case the early rapid evolution of nitrogen trioxide was observed. The slowness of decomposition of nitrosylsulphuric acid at the lower temperatures is undoubtedly due to the stabilising influence of sulphuric acid, which is a secondary product of the reaction. The decomposition of the acid begins at 73°, when it begins to melt.

The general conclusion to be drawn from the results is that the mode of decomposition suggested by Michaelis is in accord with the experimental facts. It must be pointed out, however, that (1) sulphuric acid is produced by the decomposition and tends to prevent further loss of nitrogen trioxide on heating, and (2) water escapes from the reaction zone in the early part of the heating; consequently the nitrous acid content of the residue would be expected to exceed the theoretical value.

FIG. 1.



Solubility of Nitrosylsulphuric Acid in Sulphuric Acid.—The general method of solubility determinations was adopted, the nitrosylsulphuric acid in excess being agitated with sulphuric acid of known concentration contained in thin glass tubes in a thermostat. Each tube was protected against the ingress of moisture by running the stirrer through a glass tube sealed with petroleum jelly. The sulphuric acid used was of concentrations 56·7, 62·1, 73·1, 74·9, 84·1, 90·4, and 99·8%.

After 3 hours, a sample was filtered through glass wool into a weighing bottle containing sulphuric acid and, after weighing, the contents were made up to 100 c.c. with sulphuric acid, the nitrous acid then being estimated by a method specially devised for this work. At the higher temperatures and with the lower concentrations of sulphuric acid, some of the solutions contained free nitrous acid (*i.e.*, not combined as nitrosylsulphuric acid). In order to determine the amount of the latter acid actually present, this

free nitrous acid was removed by rapid blowing with air followed by immersion in the thermostat for 15 minutes. The sample was then taken in the usual way. The results here given are also shown graphically in the figure.

Conc. of H_2SO_4 (%).	56·7	62·1	73·1	74·9	84·1	90·4	99·8	Temp.
Solubility of nitrosyl-	—	11·9	17·3	19·7	30·5	35·1	—	0·0°
sulphuric acid as per	19·3	22·6	27·0	31·4	42·4	49·2	62·0	20·9
100 g. of solution.	29·9	34·3	39·4	40·8	50·2	58·5	66·1	37·3
	35·6	39·3	46·0	46·2	56·5	61·6	67·8	49·6

TECHNICAL COLLEGE, CARDIFF. [*Received, October 14th*, 1925.]

CLIX.—*Unsymmetrically Substituted Dinitro- and Diamino-derivatives in the Stilbene and Tolane Series. Part II. The Mode of Addition of Water to 3 : 4′-Dinitro- and Diamino-tolanes.*

By HAROLD AINSWORTH HARRISON.

IN a former communication (this vol., p. 577) it was shown that two nitro-groups unsymmetrically situated in the two benzene nuclei of stilbene exert a definite influence on the reactivity of chlorine atoms attached to the carbon atoms in the side chain. The experiments now described indicate that similar influences are discernible in the unsymmetrically substituted dinitro- and diamino-tolanes, as exemplified by the mode of addition of the elements of water to the triple bond. Polarity considerations again appear to furnish a guide in determining the seat of reactivity.

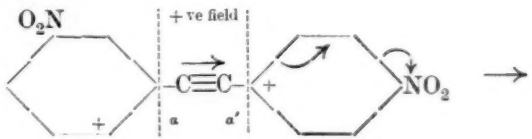
3 : 4′-*Dinitrotolane* (I) was obtained from the dichloride or dibromide of 3 : 4′-dinitrostilbene, or from α-chloro-4 : 3′-dinitrostilbene, by the action of alcoholic potassium hydroxide. In the preparation from the dibromide, although traces of the stilbene were undoubtedly produced by loss of bromine (compare Pfeiffer and Kramer, *Ber.*, 1913, **46**, 3655), no difficulty was experienced in obtaining the pure tolane.

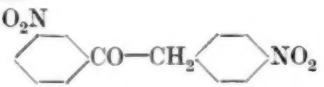
3 : 4′-Dinitrotolane assumed the elements of water only with great reluctance.* With the nitro-groups in these positions it was to be expected from the alternating polarity rule that harmonious combination of directing influences would exist, tending to make such a configuration exceedingly reactive and prone to attack at

* All the ortho-substituted nitrotolanes prepared by Reinhardt (*Ber.*, 1913, **46**, 3598), by Pfeiffer and Kramer (*ibid.*, 1913, **46**, 3655), and by Pfeiffer (*Annalen*, 1916, **411**, 72) take up the elements of water with remarkable ease. It is significant, however, that neither Reinhardt nor Pfeiffer mentions the addition of water to 4 : 4′-dinitrotolane.

the carbon atoms in the side chain. But no such enhanced reactivity was manifested and the yield of 3-nitrophenyl 4-nitrobenzyl ketone (II) was small. Robinson, Allan, Oxford, and Smith (this vol., p. 401) recognise the existence of two quite distinct effects when a nitro-group is attached to the benzene ring: the one arising from the conjugation of the nitroxyl with the nucleus and resulting in positive charges on the ortho- and para-carbon atoms, and the other a general electrical effect over the nucleus and the side chain. Applying these conceptions to 3 : 4′-dinitrotolane, one deduces respectively that a smaller density of electrons exists in the region of the two carbon atoms marked + than in the region of their immediate neighbours, and that the acetylenic carbon atoms $\alpha\alpha'$ are under the influence of a strong positive field, which inhibits reactivity towards positive ions at both centres. Since, however, the positive charge in the *p*-nitrophenyl group is nearer the acetylenic bond than is that in the *m*-nitrophenyl group, the electrons of the acetylenic bond will be displaced in the direction of the arrow, that is, from $\alpha \longrightarrow \alpha'$.* Addition of water, therefore, though difficult, takes place as follows:

(I.)





(II.)

It is also possible that the *p*-nitrophenylacetylene group is a conjugated system, but the existence of such conjugation could only be disclosed by experiments with anionoid reagents.

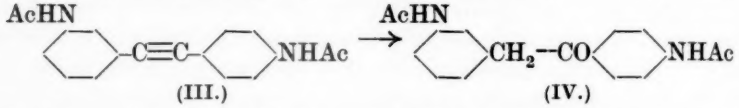
An attempt to investigate the influence of the amino-groups on the elimination of hydrogen chloride from 3 : 4′-diaminostilbene dichloride was unsuccessful, owing to the impossibility of retaining the chlorine atoms in the molecule during the reduction; 3 : 4′-*diaminostilbene* was the sole product.†

3 : 4′-*Diaminotolane*, like the nitrotolane, was very reluctant to assume the elements of water; this inertness is at first sight the more surprising in view of the peculiar ease with which 4 : 4′-diaminotolane passes into the deoxybenzoin, warm dilute hydrochloric acid

* Similar cases have been considered by Lucas and his colleagues (*J. Amer. Chem. Soc.*, 1924, **46**, 2475; 1925, **47**, 1459, 1462).

† Replacement of the chlorine atoms by hydrogen does not occur, since 3 : 4′-*diaminodibenzyl* (prepared for purposes of comparison) coincided with none of the products obtained during the whole investigation.

effecting its quantitative conversion (Reinhardt, *Ber.*, 1913, **46**, 3598). Under no conditions * did sulphuric acid bring about the corresponding reaction in the case of 3 : 4′-diaminotolane; during one reduction experiment only, in which zinc and hydrochloric acid were employed, was a small amount of *4-aminophenyl 3-aminobenzyl ketone* produced. From the *diacetyl* derivative of the aminotolane (III), however, the action of concentrated sulphuric acid resulted in the formation of the *diacetyl* derivative of this ketone (IV) in good yield, its constitution being inferred from its non-identity with *3-acetylaminophenyl 4-acetylaminobenzyl ketone*, prepared from the corresponding nitrophenyl nitrobenzyl ketone (this vol., p. 579).



(III.) (IV.)

The conception of combined general and alternating polar effects again proves valuable here. Electronic repulsion from the two acetylamino-groups, resulting from their conjugation with the respective benzene nuclei, produces a strongly negative field in the region of the acetylenic carbon atoms, which are consequently in a highly reactive state. Addition of water thus takes place with great ease.

The mechanism of reaction of the free aminotolane, on the other hand, is obscured by salt formation, but to account for the great difference in reactivity between 4 : 4′- and 4 : 3′-diaminotolane it is only necessary to suppose that the former exists in hydrochloric acid as its mono-acid salt, and the latter as its di-acid salt. In fact, the author ventures to suggest that the diquaternary ammonium base derived from 4 : 4′-diaminotolane would assume the elements of water with great difficulty.

Experimental.

3 : 4′-*Dinitrostilbene Dibromide*.—Finely-divided 3 : 4′-dinitrostilbene (21·6 g.) (this vol., p. 580) was suspended in chloroform (1 litre), bromine (12 c.c.) added, and the whole kept during 2—4 days. The stilbene gradually dissolved and later the dibromide partly crystallised. The solvent and excess of bromine were then distilled off, and the solid residue † was recrystallised from boiling glacial acetic acid (about 925 c.c.). The yield was 90%. As with the dichloride, two forms could be obtained by fractional crystallisation. The pure α-form is sparingly soluble in acetic acid,

* The concentration and temperature were varied over a wide range.

† This, unlike the dichloride (this vol., p. 581), did not char during removal of the last few c.c. of solvent.

crystallising in almost white, thick prisms, m. p. 234° (Found: Br, 36·9. $C_{14}H_{10}O_4N_2Br_2$ requires Br, 37·2%). Its production seems to be favoured by longer exposure of the chloroform solution to daylight. The pure β-form is more soluble in acetic acid or chloroform, crystallising from the former solvent in pale brown, minute plates, m. p. 214° (Found: Br, 36·95%). Both forms are sparingly soluble in most organic solvents; they separate from boiling nitrobenzene in small prisms. Even the β-form, which in substances of this type usually reacts differently from the α- form (compare Pfeiffer, *Ber.*, 1912, **45**, 1810), on being heated with pyridine at 90° for 2 hours loses both bromine atoms, reverting to the stilbene.*

3 : 4′-*Dinitrotolane* (I).—The mixture of dibromides (22·8 g.) was suspended in boiling alcohol (220 c.c.), and a solution of potassium hydroxide (6·6 g.) in water (15 c.c.) added. After being boiled under reflux for 1 hour, the mixture was allowed to cool to 50° and the brown solid filtered off. After being well washed with cold alcohol and then with water, the product was crystallised twice from glacial acetic acid, and then from a large volume of alcohol to free it from traces of stilbene (see p. 1232). The pure tolane melted at 173—174°; the yield was 70% (Found: C, 62·3; H, 3·2. $C_{14}H_8O_4N_2$ requires C, 62·7; H, 3·0%). It is easily soluble in hot benzene, nitrobenzene, acetone, or ethyl acetate, less readily in acetic acid or chloroform, somewhat sparingly soluble in ethyl alcohol, and very sparingly soluble in carbon tetrachloride, carbon disulphide, ether, or light petroleum. It produces a deep red solution in strong sulphuric acid.†

Addition of water. The nitrotolane (1 g.), obtained in a fine state of division by pouring an alcoholic solution into water, was dissolved in cold concentrated sulphuric acid. After being maintained at 15° for 30 minutes,‡ the solution was slowly poured on to ice, and the slightly resinous deposit filtered off and dissolved in acetone. Slow evaporation of the solvent left behind dark glistening plates, which after three crystallisations from alcohol (charcoal) melted at 101°, alone or mixed with an authentic specimen of 3-nitrophenyl 4-nitrobenzyl ketone (this vol., p. 582). Although the yield was only fair, no other product was isolated.

* Unlike the dibromide of the parent substance (Limpricht, *Annalen*, 1868, **145**, 338), 3 : 4′-dinitrostilbene dibromide does not yield the corresponding benzil when heated with water under pressure, even at 215° for 60 hours.

† Compare the bluish-violet colour given under similar conditions by 2 : 4-dinitrotolane (Pfeiffer, *loc. cit.*).

‡ Any other conditions, such as alteration of temperature, use of solvents, change in concentration or duration, resulted in a charred product or recovery of the unchanged nitrotolane.

3 : 4′-*Diaminostilbene.*—A solution of the dinitrostilbene (2 g.) in boiling acetic acid (15 c.c.) was cooled to 70° and zinc dust (10 g.) and hydrochloric acid (40 c.c.) were gradually added with stirring; the reaction was complete in ¾ hour. The boiling solution was filtered, and, on cooling, the *hydrochloride* separated in yellow, pearly plates or needles.* The free amine after recrystallisation from alcohol formed small, yellow plates or needles, m. p. 156° (Found : C, 80·0; H, 6·9. $C_{14}H_{14}N_2$ requires C, 80·0; H, 6·7%). It is very soluble in ethyl acetate or acetone, less readily in alcohol, ether or benzene, and sparingly soluble in chloroform, carbon tetrachloride, carbon disulphide or light petroleum. The *diacetyl* derivative crystallises from methyl alcohol in clumps of needles, m. p. 226—227° (Found : C, 73·3; H, 6·3. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·1%). This derivative is very soluble in ethyl acetate, soluble in acetone or alcohol, and sparingly soluble in benzene or chloroform. It gives no colour with cold concentrated sulphuric acid.

3 : 4′-*Diaminodibenzyl.*—The diaminostilbene (1·2 g.) was reduced with sodium (2 g.) in boiling ethyl alcohol (30 c.c.), the reaction being complete in ½ hour. When cold, the opaque solution was acidified with dilute hydrochloric acid and a small amount of tar removed by extraction with ether. The free base crystallised from the warm solution on addition of dilute sodium hydroxide (weight of crude product = 0·95 g.), and when recrystallised from aqueous alcohol formed small, white plates, m. p. 73—75°. It is easily soluble in acetone, alcohol, ether or benzene; the *hydrochloride* is readily soluble in water, from which it crystallises in needles. The *diacetyl* derivative crystallises from aqueous alcohol in small clusters of thick needles, m. p. 177° (Found : C, 72·7; H, 6·9. $C_{18}H_{20}O_2N_2$ requires C, 73·0; H, 6·8%). It is readily soluble in alcohol, acetone, or ethyl acetate, moderately easily soluble in hot chloroform, and almost insoluble in benzene. It gives no colour with cold sulphuric acid.

Reduction of 3 : 4′-*Dinitrostilbene Dichloride.*—3 : 4′-Diaminostilbene was also obtained, though with difficulty, from 3 : 4′-dinitrostilbene dichloride by reduction in alcoholic solution with zinc and hydrochloric acid at 15°.† The reduction was incomplete, and the light brown *substance* which remained after filtration of the normal reaction product, when crystallised from alcohol melted

* It is essential to isolate this amine as its hydrochloride, otherwise the melting point varies over a range of 50°.

† No reduction took place with iron powder and calcium chloride, whilst stannous chloride and acetic acid yielded a mixture of products exceedingly difficult to purify.

at 202—205° (Found: C, 65·2; H, 3·0%). It contained chlorine, but gave an immediate intense purple colour with cold concentrated sulphuric acid, and was therefore not the unchanged dichloride (see this vol., p. 582). On the other hand, it could not be diazotised. Its constitution was not further investigated.

Reduction of α-Chloro-4 : 3′-dinitrostilbene.—Facile reduction occurred when crystalline stannous chloride (25 g.) in 80% acetic acid (25 c.c.) was added to the chlorostilbene (5 g.) dissolved in boiling glacial acetic acid (50 c.c.). The solution was almost neutralised with sodium hydroxide,* and the tin precipitated by hydrogen sulphide. The filtrate was boiled and neutralised, and the free ketonic base recrystallised several times from alcohol (charcoal); after purification, it formed rosettes of almost colourless needles, m. p. 153°, which were not identical with 3 : 4′-diaminostilbene, m. p. 156°, obtained from the dichloride (see above), since an intimate mixture melted about 15° below this temperature.

A better yield of the diacetyl derivative of this base was obtained by shaking the crude reduction liquor, while still warm, with acetic anhydride in presence of sodium acetate. After standing over-night, the solution was poured into water and the suspended solid extracted with methyl ethyl ketone. The ketone layer, which separated after the addition of a large quantity of calcium chloride, was dried over potassium carbonate, the solvent removed, and the diacetyl compound recrystallised three times from methyl alcohol with the addition of ether; it then melted at 204°. (The properties of these two compounds are described below.)

3 : 4′-*Diaminotolane.*—The nitrotolane (3 g.) was boiled with alcohol (25 c.c.), and the suspension quickly cooled to 10°. Zinc dust (5 g.) was added, and then, very slowly, hydrochloric acid (17 c.c.) † during 1 hour, the temperature being maintained at 10—15°. The solution of the hydrochloride was filtered from much (2 g.) unreduced nitrotolane and the precipitated amine was extracted with ether and recrystallised from aqueous alcohol, when it formed light brown needles, m. p. 124—125° (Found: C, 80·6; H, 6·1. $C_{14}H_{12}N_2$ requires C, 80·8; H, 5·8%). It dissolves easily in alcohol, ether, ethyl acetate or acetone, rather less readily in hot benzene or chloroform, and is sparingly soluble in carbon disulphide or light petroleum. It is not converted into the deoxybenzoin by boiling with hydrochloric acid. Its *diacetyl* derivative crystallises from methyl alcohol in thick needles, m. p. 226° (Found: C, 73·8;

* The free amine appears to be somewhat unstable to hydrogen sulphide in presence of alkali; possibly a sulphur atom is incorporated in the molecule (compare Jones and Robinson, J., 1917, **111**, 911).

† Zinc and acetic acid give coloured by-products.

H, 5·55. $C_{18}H_{16}O_2N_2$ requires C, 74·0; H, 5·5%). This diacetyl derivative, unlike those of diaminostilbene (m. p. 226—227°) and diaminodibenzyl (m. p. 177°), gives an immediate red colour with cold concentrated sulphuric acid.

4-*Acetylaminophenyl* 3-*Acetylaminobenzyl Ketone* (IV).—Pure 3 : 4′-diacetyldiaminotolane (III) (0·3 g.) was dissolved in cold concentrated sulphuric acid (3·0 c.c.), and the temperature maintained at 15° for ½ hour. No hydrolysis took place under these conditions. The deep red solution was then poured on to ice, and the mauve-coloured solid at once filtered off. It slowly changed to a grey non-crystalline mass, which by purification from alcohol was transformed into almost white needles, m. p. 204° (Found : C, 69·3; H, 6·1. $C_{18}H_{18}O_3N_2$ requires C, 69·7; H, 5·8%). The yield was good, and no other product was detected. This diacetyl compound was identical with that obtained from the reduction of α-chloro-4 : 3′-dinitrostilbene (see above). It is soluble in alcohol, dilute acetic acid, or ethyl acetate, but sparingly soluble in ether. It no longer gives a red colour with cold concentrated sulphuric acid.

4-*Aminophenyl* 3-*Aminobenzyl Ketone.*—During the course of one experiment on the reduction of 3 : 4′-dinitrotolane with zinc and hydrochloric acid at 70—80°, after separation of the hydrochloride of the normal reduction product, precipitation of the mother-liquors with alkali yielded a brown solid which, after being twice crystallised from aqueous alcohol, melted at 156°. Its melting point was depressed 20° by admixture of an authentic specimen of 3 : 4′-diaminostilbene (m. p. 156°),* but not at all by addition of the amine (m. p. 153°) formed on reduction of α-chloro-4 : 3′-dinitrostilbene; its diacetyl derivative, m. p. 204°, was identical with that obtained by the action of sulphuric acid on 3 : 4′-diacetyldiaminotolane. Without doubt it was a deoxybenzoin produced by addition of water to the triple bond of the tolane, probably under the influence of the metal, since boiling hydrochloric acid alone effected no change (Found : C, 74·0; H, 6·4. $C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2%). This amine is soluble in all the usual organic solvents, and crystallises in clusters of slightly brown, flat needles from alcohol.

3-*Acetylaminophenyl* 4-*acetylaminobenzyl ketone* was obtained when the corresponding dinitro-ketone (1·3 g.) was reduced at 10° with zinc and hydrochloric acid, as in previous experiments. The crude amine isolated from the hydrochloride was at once acetylated, and the product recrystallised from alcohol, when it melted at 184—186° (Found : C, 69·35; H, 6·0. $C_{18}H_{18}O_3N_2$ requires C, 69·7; H, 5·8%). The solubilities of this diacetyl derivative were similar to those of

* Which even under these conditions, therefore, is not produced (compare Reinhardt, *loc. cit.*).

the isomeric ketone, m. p. 204°, but a mixture of the two melted at 170—179°. This dissimilarity definitely establishes the constitution of 4-acetylaminophenyl 3-acetylaminobenzyl ketone, and consequently the mode of addition of water to 3 : 4′-diaminotolane and to its diacetyl derivative.

In conclusion, the author wishes to thank Professor Lapworth for suggesting the research, and the Research Fund Committee of the Chemical Society for a grant which has defrayed part of the expenses.

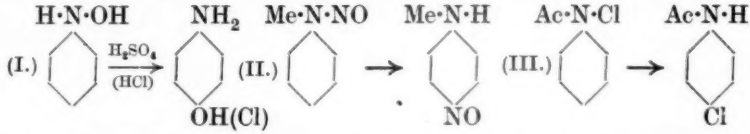
THE UNIVERSITY, MANCHESTER. [*Received, January 4th*, 1926.]

CLX.—*Investigations in the Diphenyl Series. Part I. Migration Reactions.*

By FRANK BELL, JOSEPH KENYON, and PERCY HARRY ROBINSON.

IN view of the appearance of a paper by Vorländer (*Ber.*, 1925, **58**, 1913), in which 4-hydroxylaminodiphenyl is described, and of another by Scarborough and Waters on the chlorination and bromination of 4-aminodiphenyl (this vol., p. 557), it has been thought advisable to communicate some of the results already obtained by the authors in the same field.

The literature shows that numerous attempts have been made to elucidate the spatial relations of the two nuclei in diphenyl compounds, and there is considerable evidence in favour of the view of the closeness of the 4, 4′-positions in some derivatives. If the 4, 4′-positions in diphenyl are close together, there is a reasonable probability that those types of reactions which involve the para-migration of certain groups in simple benzene compounds might also be exhibited, under appropriate conditions, by certain derivatives of diphenyl, the migrating group passing from position 4 to position 4′. Migration reactions in the diphenyl series analogous to the following have been looked for, but have not been found :



In the corresponding diphenyl compounds decomposition occurs in case (II), whilst in cases (I) and (III) migration does take place, not, however, to the 4′-position but most probably to the adjacent 3-position.

There is an extensive literature on the preparation of diphenyl by the thermal decomposition of benzene, the most recent account being that of Lowe and James (*J. Amer. Chem. Soc.*, 1923, **45**, 2666), who, however, used an apparatus which is outside the resources of an ordinary laboratory. A simpler device is described in the experimental part; chlorobenzene, under similar treatment in the apparatus described, underwent extensive carbonisation, and no 4 : 4′-dichlorodiphenyl was obtained. The nitration of diphenyl was carried out by a modification of the methods due to Hübner (*Annalen*, 1881, **209**, 339) and Van Hove (*Bull. Soc. chim. Belg.*, 1923, **32**, 52).

By the reduction of 4-nitrodiphenyl with aluminium amalgam and moist ether, there is obtained a complex mixture of 4-azodiphenyl, 4-azoxydiphenyl, 4-aminodiphenyl, and 4-hydroxylaminodiphenyl, together with unchanged nitrodiphenyl. By crystallisation of this mixture from benzene, a 30% yield of 4-hydroxylaminodiphenyl is obtained. Vorländer (*loc. cit.*), who gives no experimental details whatever, states that the compound was prepared " nach bekanntem Verfahren " and melted at 132—134°.

The insolubility of 4-hydroxylaminodiphenyl militates seriously against migration experiments under favourable conditions. Sulphuric acid of various concentrations was employed at first, but as the minimum concentration of this acid necessary for solution of the hydroxylamino-compound at the ordinary temperature is above 50%, deep-seated decomposition occurs, and no crystalline material other than 4-azoxydiphenyl can be isolated from the products of the reaction. By the action of 10% sulphuric acid at 100°, a very small proportion of a new compound was formed. This substance has not yet been thoroughly investigated, but it is believed to be 4-diphenylyl(4-amino-3-diphenylyl)amine,

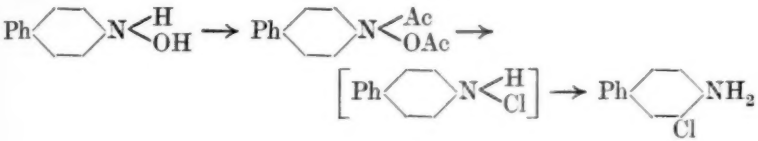
$$C_6H_4Ph\cdot NH\cdot C_6H_3Ph\cdot NH_2.$$

When hydrogen chloride is passed into a dry ethereal solution of 4-hydroxylaminodiphenyl, or when this compound is left for some time in contact with strong hydrochloric acid, *4-hydroxylaminodiphenyl hydrochloride* is formed, which, on heating, decomposes to give principally 4-azoxydiphenyl.

An alcoholic solution of hydrogen chloride converts 4-hydroxylaminodiphenyl almost completely into 4-azoxydiphenyl, but at the same time there is produced a very small proportion of a compound which melts at 69° and contains chlorine.

Acetyl chloride reacts readily with 4-hydroxylaminodiphenyl to yield a diacetyl derivative believed to be *diacetyl-4-hydroxylaminodiphenyl*. This compound can be prepared in almost theoretical yield by dissolving 4-hydroxylaminodiphenyl in warm acetic

anhydride, and when warmed with strong hydrochloric acid it undergoes hydrolysis and simultaneous conversion into a chloro-base (m. p. 69°), the hydrochloride of which hydrolyses very readily, and in consequence has not been prepared in a sufficiently pure state for analysis. The chloro-base yields a monoacetyl derivative of m. p. 146° which is identical with that obtained by the action of acetic acid on diphenylyl-4-acetylchloroamine (*vide* below), so that the course of this reaction is probably expressed by the following scheme :



4-*Methylaminodiphenyl* was prepared by treating 4-acetylaminodiphenyl with sodium and methyl iodide with subsequent elimination of the acetyl group, and was purified by conversion into its nitroso-derivative.

4-*Nitrosomethylaminodiphenyl*, both alone and when suspended in ether (in which it is only sparingly soluble), was mixed with an alcoholic solution of hydrogen chloride, when slow reaction ensued with evolution of gas. No nitroso-4-methylaminodiphenyl was found in the reaction mixture, which consisted mainly of 4-methylaminodiphenyl together with a little of the unchanged substance.

4-*Diazomethylaminodiphenyl* is a by-product in the preparation of 4-nitrosomethylaminodiphenyl from the crude secondary amine, which probably contains a little 4-aminodiphenyl.

Diphenylyl-4-acetylchloroamine. It is clear from the literature that the preparation of aryl acyl chloroamines is susceptible to slight variations in experimental conditions (compare Armstrong, J., 1900, **77**, 1047; Chattaway and Orton, J., 1901, **79**, 275).

A similar susceptibility has been found in the case of 4-acetylaminodiphenyl, which, however, reacts rapidly and quantitatively at 70—80°. One sample yielded 67% of diphenylyl-4-acetylchloroamine after only 10 minutes' heating. Further, the state of subdivision is very important, and may account for the difficulties met with by Armstrong and his students in the case of acetanilide (*loc. cit.*). When the 4-acetylaminodiphenyl was powdered mechanically, the yields were poor.

When diphenylyl-4-acetylchloroamine is warmed with glacial acetic acid it is transformed into a chloro-4-acetylaminodiphenyl believed to be 3-chloro-4-acetylaminodiphenyl (compare above).

No trace of 4′-chloro-4-acetylaminodiphenyl was detected, although its presence was specially sought.

3-Chloro-4-acetylaminodiphenyl results directly if the sodium hypochlorite solution used is above normal in strength.

A quantitative yield of 3-chloro-4-acetylaminodiphenyl results also from the direct chlorination of 4-acetylaminodiphenyl in acetic acid. Again no trace of 4′-chloro-4-acetylaminodiphenyl was detected. This is in marked contrast with the bromination of 4-acetylaminodiphenyl in acetic acid, which yields 30% of the theoretical quantity of 4′-bromo-4-acetylaminodiphenyl together with 65% of a bromo-base (m. p. 65°) not yet fully examined.

Experimental.

Diphenyl.—The heating coil, which consists of about 1 yard of 32 gauge nichrome wire, is loosely threaded through a strip of mica 5″ × 1¼″ and suspended in the neck and body of a 5-litre flask fitted with an upright condenser. Benzene (1½ litres) is placed in the flask and boiled. When benzene is dripping freely from the condenser, the current is switched on, and by means of a sliding resistance is gradually raised to the value (about 3 amps.) at which the flask begins to fill with fumes. Little attention is required, and at the end of about 30 hours the liquid is transferred to a flask and distilled. Benzene comes over first, and then the temperature rises rapidly. The fraction b. p. 245—260° is collected and crystallised from alcohol. The yield of pure diphenyl averages 9 g. per hour.

Nitration of Diphenyl.—To a solution of diphenyl in acetic acid (2 parts) at 70—90°, nitric acid (*d* 1·51; 2½—3 mols.) is added in small quantities. The solution darkens, and when about one-third of the acid has been added a visible and steady reaction sets in. The remaining acid is added more carefully, the experiment taking 1¼ to 1½ hours from the first addition of acid. After cooling, the crystalline crop of 4-nitrodiphenyl is filtered off, and the filtrate diluted with water. The oily layer thus precipitated is separated roughly from the aqueous layer and filtered from a further amount of 4-nitrodiphenyl. The oil is heated in a current of steam to free it from residual acid and unchanged diphenyl, and then distilled in a vacuum. Moisture and a trace of diphenyl come over first, and the main bulk distils at 188—193°/20 mm. The distillate is dissolved in alcohol at 40° and the crystals of 4-nitrodiphenyl which separate on cooling are filtered off. After evaporation of the alcohol, 2-nitrodiphenyl crystallises in characteristic large plates or prisms. 100 G. of diphenyl give 60—70 g. of 4-nitrodiphenyl, m. p. 114°, and 35—39 g. of 2-nitrodiphenyl, m. p. 35—37°.

4-*Hydroxylaminodiphenyl.*—A solution of 4-nitrodiphenyl (50 g.) in ether (1300 c.c., previously distilled from sodium hydroxide) is cooled in a freezing mixture and to it is added aluminium amalgam (10 g.), in very thin sheets, at such a rate that the reaction does not become too vigorous; the reaction vessel is shaken from time to time. Very little hydrogen is evolved if the mixture is kept cold, and the amalgam takes about 2 hours for complete reaction. The mixture is then filtered, the bulky aluminium hydroxide washed several times with dry ether, and the filtrate and washings are evaporated to dryness. The residue is dissolved in the minimum amount (about 250 c.c.) of boiling benzene, and the yellow solution allowed to cool. 4-Hydroxylaminodiphenyl separates in almost colourless, glistening leaflets which appear to fill the whole bulk of the liquid. These are filtered off and dried (yield, 10—14 g.). The compound melts at 152—154° to a red liquid which sets, and in turn melts at 188—190° (Found: C, 77·8; H, 6·0; N, 7·7. $C_{12}H_{11}ON$ requires C, 77·8; H, 5·9; N, 7·6%).

The formation of a deep damson colour with concentrated sulphuric acid is a sensitive reaction for this compound.

4-Hydroxylaminodiphenyl (2 g.) was maintained in the molten state for 30 minutes, and the cooled residue (1·86 g.) dissolved in boiling benzene. The solution on cooling deposited crystals of 4-azodiphenyl, and after evaporation of the benzene, the residue consisted of a mixture of 4-azoxydiphenyl (m. p. 211—212°) and 4-aminodiphenyl (m. p. 52°).

On treatment of an ethereal solution of 4-hydroxylaminodiphenyl with hydrogen chloride or by leaving a suspension in concentrated hydrochloric acid for some time, the *hydrochloride* is obtained as a white powder (Found: HCl, 16·6. $C_{12}H_{11}ON,HCl$ requires HCl, 16·5%). The principal product obtained on heating the hydrochloride is 4-azoxydiphenyl.

Action of 10% *sulphuric acid.* 4-Hydroxylaminodiphenyl (5 g.) is triturated with sulphuric acid (600 c.c. of 10%), and the mixture heated on a steam-bath until the whole assumes a deep chocolate colour. It is then filtered hot, and the insoluble residue extracted with 2 litres of boiling water. The filtrates deposit amine sulphates, which are filtered off and suspended in sodium carbonate solution. The mixture is boiled and, after addition of some alcohol, filtered from a trace of impurity. On cooling, the liquid fills with fine, silky crystals, which are filtered off and crystallised from aqueous alcohol; m. p. 156°. It is difficult to make certain that the product is quite free from 4-aminodiphenyl, since the sulphate of this compound must be present in the filtrate. As the compound is insoluble in sodium hydroxide, it is tentatively suggested that it

may be produced by the *o*-semidine change of an intermediate reactive 4-hydrazodiphenyl (Found : C, 85·0; H, 6·1. $C_{24}H_{20}N_2$ requires C, 85·6; H, 6·0%).

By the action of an alcoholic solution of hydrogen chloride on the hydroxylamine there was obtained a small quantity of a chloro-base, m. p. 69° (see below).

Diacetyl-4-hydroxylaminodiphenyl was prepared by dissolving 4-hydroxylaminodiphenyl in acetic anhydride and pouring the solution, filtered from a little 4-azoxydiphenyl, into excess of water. The well-washed precipitate crystallised from alcohol in clusters of short, thick needles, m. p. 119° (Found : C, 71·2; H, 5·8; N, 5·2. $C_{16}H_{15}O_3N$ requires C, 71·4; H, 5·6; N, 5·2%).

This compound gives a deep damson colour with concentrated sulphuric acid. This diacetyl derivative (24 g.) was dissolved in 90 c.c. of concentrated hydrochloric acid by warming on a water-bath, 500 c.c. of water were added, and the whole was filtered while boiling. The hydrochloride which separated on cooling was difficult to purify by crystallisation, as it was so readily hydrolysed. It was decomposed by sodium carbonate, and the oil obtained was filtered off after solidification. By repeated crystallisation from aqueous alcohol, it was obtained as a constant-melting chloro-base, m. p. 69° (Found : N, 6·9. $C_{12}H_{10}NCl$ requires N, 6·9%).

It gives an acetyl derivative which crystallises from alcohol in glistening needles, m. p. 146° (Found : C, 68·4; H, 5·0; N, 6·0. $C_{14}H_{12}ONCl$ requires C, 68·4; H, 4·9; N, 5·7%).

4-*Aminodiphenyl*.—This compound is formed during the preparation of 4-hydroxylaminodiphenyl, but its separation from the accompanying azoxy-, azo-, and nitro-compounds is difficult. The benzene filtrate from 4-hydroxylaminodiphenyl was therefore evaporated to dryness, the residue finely powdered and suspended in ether, aluminium amalgam added until the ethereal solution became colourless, the filtered solution evaporated to dryness, and the residue dissolved in boiling alcohol; on cooling, 4-hydrazodiphenyl separated in colourless, glistening needles, m. p. 167—169°. This was filtered off, and by dilution of the mother-liquor 4-aminodiphenyl (m. p. 52—53°) was obtained.

4-Nitrodiphenyl is converted directly into 4-aminodiphenyl by the same process when excess of aluminium amalgam is added. This appears to be the cleanest method of preparation, and the yield is good.

4-*Hydrazodiphenyl* was heated with hydrochloric acid and sulphuric acid of various strengths, but only 4-azodiphenyl and 4-aminodiphenyl could be isolated from the products, thus confirming the observation of Rassow (*J. pr. Chem.*, 1901, **63**, 449).

4-*Azoxydiphenyl* was isolated from the product obtained by partial reduction of 4-nitrodiphenyl, by means of its ready solubility in benzene and insolubility in alcohol. It melts at 212° whether prepared by this method or by Zimmermann's (*Ber.*, 1880, **13**, 1960), who, however, gives the m. p. as 206° (Found: C, 81·8; H, 5·2; N, 8·1. Calc.: C, 82·3; H, 5·1; N, 8·0%).

4-*Azodiphenyl* (m. p. 249°) was obtained by distilling a mixture of 4-azoxydiphenyl and iron filings under reduced pressure.

4-*Methylaminodiphenyl*.—A mixture of 4-acetylaminodiphenyl (31·5 g.; m. p. 171°), dry xylene (200 c.c.), and sodium (5 g.) was heated at 130° for 2—3 hours and cooled, methyl iodide (25 g.) was added, and the reaction completed by warming for a short period. The xylene was distilled off and the residue heated under reflux with alcoholic potash for 15 hours. Alcohol and xylene were removed in a current of steam, and the residue was extracted with ether. The ethereal extract was dried with sodium sulphate and after evaporation of the ether the residue distilled almost wholly at 198—202°/20 mm., the distillate setting to a semi-solid mass. This was best purified by conversion into the nitroso-derivative, and subsequent decomposition of this by boiling with concentrated hydrochloric acid according to the following procedure. The semi-solid mass was dissolved in glacial acetic acid, and the calculated amount of sodium nitrite added. The precipitate was filtered off, dried on porous plate, and boiled with alcohol, which extracted the nitrosoamine from an insoluble yellow product (A). On cooling the filtrate, the *nitrosoamine* crystallised, and was obtained as an almost colourless, microcrystalline powder, m. p. 116°, by recrystallisation from alcohol (Found: C, 73·6; H, 5·7. $C_{13}H_{12}ON_2$ requires C, 73·6; H, 5·7%).

The nitrosoamine gave brilliant colours at the various stages of the Liebermann reaction. To obtain the secondary base, the nitroso-compound was boiled with concentrated hydrochloric acid. The *hydrochloride* thus obtained crystallised from dilute hydrochloric acid as a white powder (Found: HCl, 16·6. $C_{13}H_{13}N$,HCl requires HCl, 16·6%). On decomposition with sodium carbonate, 4-methylaminodiphenyl was obtained as an oil which rapidly solidified and had m. p. 38°. It was readily soluble in almost all organic solvents, gave an *acetyl* derivative, m. p. 118—119°, which was very soluble in alcohol and separated from aqueous alcohol in a gelatinous condition.

This base is much better characterised as its p-*toluenesulphonyl* derivative, which was readily prepared by the action of *p*-toluenesulphonyl chloride in pyridine solution, and crystallised from alcohol in lustrous, white needles, m. p. 128° (Found: N, 4·2. $C_{20}H_{19}O_2NS$ requires N, 4·2%).

Its constitution is easily checked, since it may also be prepared by shaking the *p*-toluenesulphonate of 4-aminodiphenyl with methyl sulphate and sodium hydroxide. The p-*toluenesulphonate* of 4-*aminodiphenyl*, prepared by the usual method, crystallises from alcohol in colourless needles, m. p. 160° (Found : N, 4·5. $C_{19}H_{17}O_2NS$ requires N, 4·3%).

The yellow product (A) obtained in the preparation of 4-nitrosomethylaminodiphenyl crystallised readily from benzene in splendid, lustrous, yellow plates which decomposed violently at 187°. On boiling with dilute sulphuric acid, there was vigorous evolution of nitrogen. When this had ceased, water was added and the whole filtered boiling hot. 4-Methylaminodiphenyl sulphate crystallised from the filtrate; the residue, after solution in sodium hydroxide and precipitation, melted at 164° and was identical with 4-hydroxydiphenyl prepared directly from 4-aminodiphenyl. The compound (A) must therefore be 4-*diazomethylaminodiphenyl* (Found : C, 81·8; H, 5·7; N, 11·1. $C_{25}H_{21}N_3$ requires C, 82·6; H, 5·8; N, 11·6%).

4-Diazoaminodiphenyl is formed by treating an acetic acid solution of 4-aminodiphenyl with sodium nitrite and forms yellow plates, m. p. 147° (*Ber.*, 1925, **58**, 1913).

4-Nitrosomethylaminodiphenyl both alone and when suspended in ether was treated with an alcoholic solution of hydrogen chloride. After 24 hours, the white solid was filtered off and decomposed with sodium hydroxide. The solid thus obtained was dissolved in alcohol, and on cooling, a small crop, m. p. 96°, was obtained. Although crystallisation does not alter this melting point, the product appears to be a mixture of unchanged 4-nitrosomethylaminodiphenyl and 4-methylaminodiphenyl, for, on treatment with acetic anhydride and subsequent crystallisation from alcohol, pure 4-nitrosomethylaminodiphenyl was obtained. After separation of the crop of m. p. 96°, the mother-liquor began to deposit an oil which, after purification, yielded 4-methylaminodiphenyl (m. p. 38°).

Diphenylyl-4-acetylchloroamine.—4-Acetylaminodiphenyl (31·5 g.) was dissolved in the minimum quantity of boiling alcohol, and the solution stirred rapidly into 3 litres of cold water, a paste of the consistency of whipped cream resulting. This paste was filtered off with the aid of the pump but not pressed out; it was washed with water to remove all alcohol, and then suspended in water (600 c.c.) containing potassium bicarbonate (60 g.). A considerable excess of sodium hypochlorite solution was added [equivalent to 11·6 g. of hypochlorous acid instead of 7·9 g. (calc.)], the strength of the whole mixture being 0·16*N* in respect of hypochlorous acid.

The mixture was maintained at about 70° with constant shaking for ½ hour, and then allowed to cool. The solid was filtered off and a sample extracted with chloroform. The solvent was removed by a current of air and finally by evacuation. A weighed quantity of this product was dissolved in chloroform and shaken with acetic acid and potassium iodide solution and the liberated iodine was estimated (Found : Cl, 13·9. $C_{14}H_{12}ONCl$ requires Cl, 14·4%).

This compound crystallises from chloroform–light petroleum in square plates melting at 127° if heated rapidly, and at 160° undergoes a vigorous change, presumably to 3-chloro-4-acetylaminodiphenyl.

Transformation of Diphenylyl-4-acetylchloroamine.—The main bulk of this substance was filtered off, well washed with water, dissolved in glacial acetic acid, and the solution kept at 80° for 10 minutes and cooled; the vessel then became filled with masses of colourless needles, m. p. 145°, and 147° after recrystallisation from aqueous alcohol. The final mother-liquors contained a little unchanged 4-acetylaminodiphenyl and a trace of a brown oil.

Fractional crystallisation of this substance and of the residues in the acetic acid mother-liquors failed to detect the presence of any trace of 4′-chloro-4-acetylaminodiphenyl. The compound, hydrolysed by boiling 50% sulphuric acid, gave a base which, after crystallisation from aqueous methyl alcohol, melted at 69°. 4′-Chloro-4-aminodiphenyl has m. p. 134°, so that it is highly probable that the above compound is 3-chloro-4-aminodiphenyl, and this view of its constitution is supported by its preparation by direct chlorination.

Chlorine (6·65 g.) (5% excess) was slowly bubbled through a solution of 4-acetylaminodiphenyl (21 g.) in glacial acetic acid (300 c.c.) in a tall vessel. A copious precipitate began to form at once, and after completion of the experiment 50 c.c. of water were added and the pale yellow product was filtered off. It melted at 144° and after recrystallisation from alcohol was obtained in fine, colourless needles, m. p. 146°. This substance on hydrolysis gave a base, m. p. 69°, identical with that obtained above. Exhaustive fractional crystallisation showed that the chlorination was practically quantitative, only 4% of unchanged 4-acetylaminodiphenyl being recovered and no trace of 4′-chloro-4-acetylaminodiphenyl was detected.

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BATTERSEA POLYTECHNIC, S.W. 11. [*Received, January 14th,* 1926.]

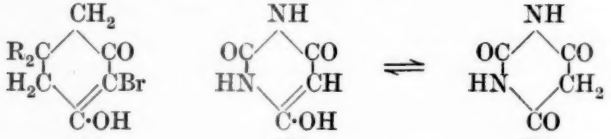
CLXI.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part XII. Halogen Compounds of Barbituric Acids.*

By ALEXANDER KILLEN MACBETH, THOMAS HENRY NUNAN, and DAVID TRAILL.

PREVIOUS work on the halogen derivatives of certain diketones has now been extended to compounds of the barbituric acid series. Baeyer (*Annalen*, 1864, **130**, 133) pointed out that there is a difference in the reactivity of the two halogen atoms in dibromobarbituric acid, one being more readily replaced than the other by hydrogen. Whiteley (J., 1921, **119**, 377) extended this observation and found that the reduction of dibromobarbituric acid is effected to the extent of one-half of the total bromine when an aqueous solution of the compound is added to a neutral solution of potassium iodide.

Hydrazine hydrate has now been found to act in a similar way, nitrogen being liberated in a volume agreeing with the reduction of one bromine atom. Similarly the chlorine atom is removed by this reagent from dichlorobarbituric acid. The corresponding halogen compounds of 1-phenylbarbituric acid and 1 : 3-diphenylbarbituric acid, as anticipated, gave results in agreement with the above observations, the reduction occurring readily in all cases.

The stability of the monohalogen derivatives of the barbituric acids may be connected with the enolic constitution of these compounds, in accordance with the explanation advanced (J., 1922, **121**, 1117, 2173) in the case of the derivatives of 1 : 1-dimethyl-*cyclo*hexane-3 : 5-dione and *cyclo*hexane*spirocyclo*hexane-3 : 5-dione (I; $R_2 = Me_2$ and $C_5H_{10}>$, respectively).

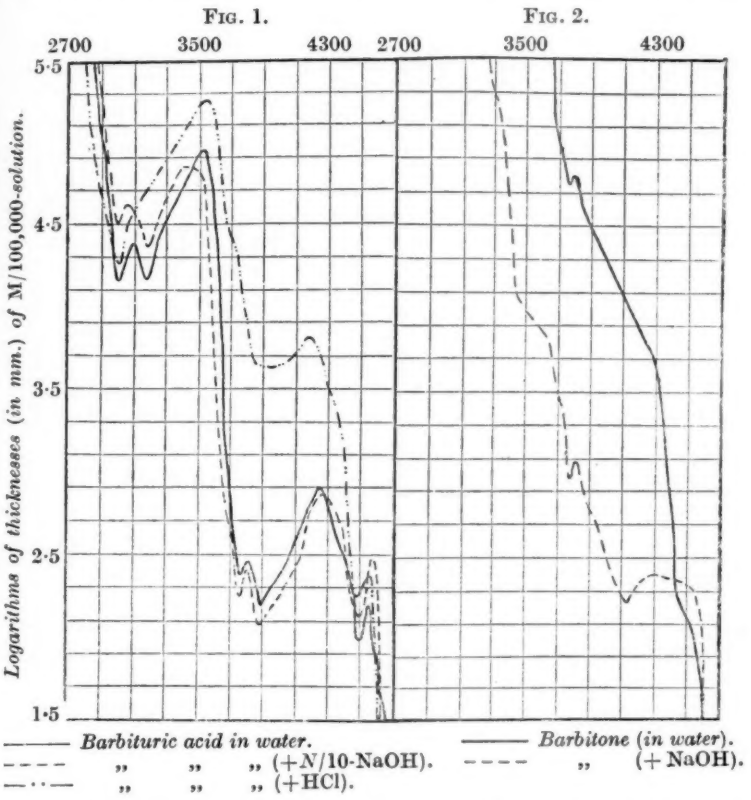


(I.) (II.) (III.)

The difference in behaviour of the dichloro-derivatives of barbituric acids and those of the other diketones previously examined (J., 1922, **121**, 1120, 2176; 1923, **123**, 1129) is of interest. In the former case one of the halogen atoms is eliminated by hydrazine hydrate, whereas in $\gamma\gamma$-dichloroacetylacetone, $\gamma\gamma$-dichlorobenzoylacetone, 4 : 4-dichloro*cyclo*hexane-3 : 5-dione, and *cyclo*hexane*spiro*-4 : 4-dichloro*cyclo*hexane-3 : 5-dione no reduction occurs. A ready explanation of this difference is obtained on the polarity basis by

considering the alternate effects of the other atoms in the barbituric acid ring, all of which act together to increase the induced electropositive character of the halogen atoms.

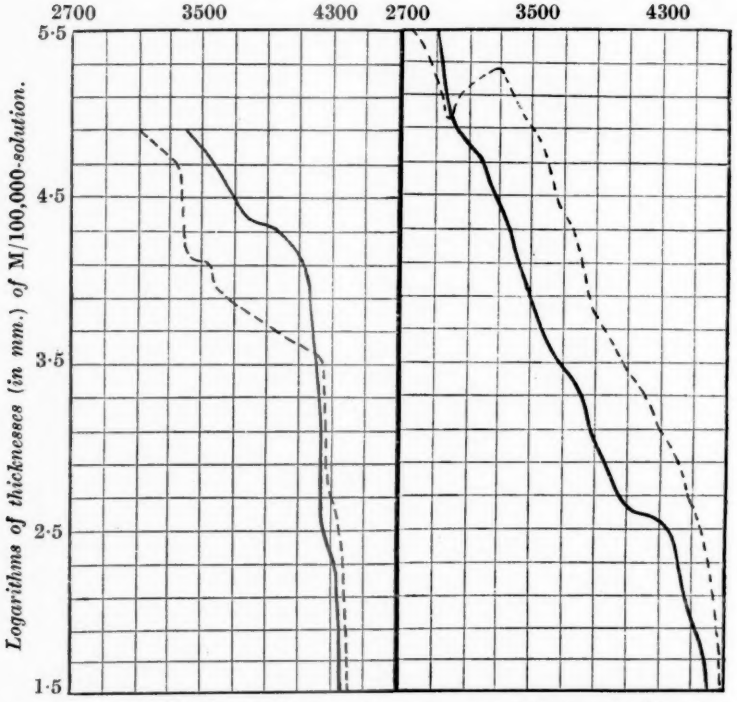
The stability of the halogen atom in the monohalogenobarbituric acids may, as has been indicated above, be explained by assuming an enolic structure for these compounds. In order to throw further light on this assumption the absorption spectra of characteristic



compounds of this class were examined. The results are shown in Figs. 1—4. The absorption of barbituric acid was examined by Hartley (J., 1905, **87**, 1796), who found that the acid transmitted a continuous spectrum very freely through thicknesses of *M*/1000-solution varying from 1—20 mm. In view of the results obtained in the past few years in absorption work, we were not surprised to find, on further examination of barbituric acid, that it showed selective absorption, its spectrum being characterised by deep complex bands extending over 1/λ 2950—3400, 3700—4200, 4450—

4530 and with heads at $1/\lambda$ 3000, 3170, 3760, 3880, 4490 approximately. The sodium salt (barbituric acid in the presence of $N/10$-sodium hydroxide) shows an absorption practically identical with that of the acid itself and therefore it is evident that in aqueous solution the acid exists in the enolised form (II). As was expected, in the presence of a strong acid the keto-enol change is induced: the absorption curve of barbituric acid in the presence of hydro-

FIG. 3. FIG. 4.



——— 5:5-*Dichlorobarbituric acid.*
- - - - *(in presence of* "N/10-NaOH)."

——— 5:5-*Dibromobarbituric acid.*
- - - - *(in presence of* "N/10-NaOH)."

chloric acid does not show to the same extent the marked selective effect characteristic of the enolic structure, the acid being present mainly in the ketonic form (III).

It was considered of interest to examine the absorption of barbitone, as the constitution of this compound is definitely fixed and it may be taken as characteristic of the *C*-dialkyl type. Its spectrum, like that of barbituric acid in the presence of hydrochloric acid, shows no selective effect characteristic of the enolic

form. In the presence of alkali, barbitone further develops the small absorption band at about $1/\lambda$ 3760, and this is probably due to enolisation involving a hydrogen atom of one of the imino-groups.

The absorption spectra of dichloro- and dibromo-barbituric acids are shown in Figs. 3 and 4. The curves are of the same type as those of barbitone, the selective effect connected with the enolic structure being absent. It has been pointed out that hydrazine hydrate reacts with the dihalogen compounds, eliminating one of the halogen atoms and forming the hydrazine salt of the resulting monohalogen derivative. No marked band development is observed in the spectra of the dihalogen compounds on the addition of sodium hydroxide, and therefore it must be inferred that, at the dilutions employed, this reagent does not react greatly with the labile halogen atoms.

The evidence of the absorption spectra of barbituric acid and its derivatives therefore clearly shows (*a*) that the parent acid exists in the enolic form in aqueous solution, whilst in acid solution the compound is present mainly as the ketonic modification; and, further, (*b*) that the dihalogen derivatives are compounds of the *C*-dihalogen type, which leaves no grounds for attributing the reactivity of the halogen atom to an oxygen-halogen linking (compare Graham and Macbeth, J., 1922, **121**, 1109, 2601). The bands found in the regions $1/\lambda$ 3000 and 3760 are probably connected with enolisation involving an imino-group, as these are found in barbitone and dibromobarbituric acid in the presence of alkali.

Experimental.

The absorption spectra recorded were all obtained with a Hilger spectroscope fitted with a camera attachment. The reductions described were carried out in a Van Slyke nitrometer, hydrazine hydrate (50% solution) being employed throughout.

Dichlorobarbituric acid. Barbituric acid, prepared by Gabriel and Coleman's method (*Ber.*, 1904, **37**, 3657), was chlorinated in aqueous suspension at 30—40°, leaflets, m. p. 219—220°, being obtained. The reaction with hydrazine hydrate is vigorous and is complete in a few seconds. 5 C.c. of a solution of 0·980 g. in 25 c.c. of alcohol liberated 11·9 c.c. of nitrogen at 10·5° and 732 mm. One g.-mol. therefore liberates 13·93 g. of nitrogen, corresponding with the removal of one chlorine atom.

The *hydrazide* of monochlorobarbituric acid is precipitated from the above reaction mixture and may also be prepared by the addition of hydrazine hydrate to an alcoholic solution of monochlorobarbituric acid. It does not melt below 300° (Found:

Cl, 18·2; N_2H_4, 16·7.* $C_4H_7O_3N_4Cl$ requires Cl, 18·4; N_2H_4, 16·6%).

Dibromobarbituric acid was prepared by Biltz and Hamburger's method (*Ber.*, 1916, **49**, 635). Recrystallised from 2*N*-nitric acid, it had only a faint rose tinge and melted at 234°. A very vigorous reaction takes place with hydrazine hydrate, and white crystals of the hydrazide of monobromobarbituric acid separate. 5 C.c. of a solution of 1·124 g. of the dibromo-compound in alcohol liberate 12·1 c.c. of nitrogen at 15° and 729·1 mm. One g.-mol. therefore liberates 14·07 g. of nitrogen, which corresponds with the reduction of one bromine atom.

The *hydrazide* of monobromobarbituric acid, isolated above, may also be prepared directly from monobromobarbituric acid. It does not melt below 300° (Found: Br, 33·8; N_2H_4, 13·3. $C_4H_7O_3N_4Br$ requires Br, 34·0; N_2H_4, 13·5%).

Monobromobarbituric acid, prepared by Biltz and Hamburger's method (*loc. cit.*), showed no reduction with hydrazine hydrate at the laboratory temperature.

5 : 5-*Dibromo*-1 : 3-*diphenylbarbituric acid*, prepared by Whiteley's method (J., 1907, **91**, 1367), reacts vigorously with hydrazine hydrate with the elimination of one bromine atom. 0·438 G. of the dibromo-compound liberated 12·6 c.c. of nitrogen at 13° and 719·8 mm. on treatment with hydrazine hydrate. One g.-mol. liberates 14·2 g. of nitrogen, which is in fair agreement with the removal of one halogen atom.

The *hydrazide* of 5-bromo-1 : 3-diphenylbarbituric acid separates during the above reaction as a creamy solid which recrystallises from alcohol in small needle-shaped laths; these appear as arborescent aggregates under the microscope; m. p. 220° (Found: Br, 21·6; N_2H_4, 8·3. $C_{16}H_{15}O_3N_4Br$ requires Br, 21·8; N_2H_4, 8·5%).

5-*Bromo*-1 : 3-*diphenylbarbituric acid*, prepared by Whiteley's method (J., 1921, **119**, 378), was not reduced by hydrazine hydrate, but formed the above hydrazide.

1-*Phenylbarbituric acid* was prepared on lines parallel to those followed in the preparation of the diphenyl acid. Phosphoryl chloride (60 g.), malonic acid (20 g.), and phenylcarbamide (25 g.) were heated under reflux for 6 hours with dry chloroform (200 c.c.) at a temperature just below the boiling point. After removal of the chloroform in a current of air, the residual syrup was left in alcohol to decompose the phosphoryl chloride and then poured on ice. The solution of the creamy solid in sodium carbonate was filtered, and acidified with hydrochloric acid. The resulting solid

* Estimated by a modification of Rimini's method (see J., 1925, **127** 897).

was gently heated with a little alcohol to remove the soluble acetylated products, and after crystallisation from alcohol had m. p. 262° (Found: N, 13·7. $C_{10}H_8O_3N_2$ requires N, 13·7%).

3 : 3-*Dibromo*-1-*phenylbarbituric Acid.* — Phenylbarbituric acid (5 g.) was heated on a water-bath with glacial acetic acid (50 c.c.) * and dissolved on the gradual addition of the theoretical amount of bromine. The solution, after further heating (30 minutes), was poured on ice. Repeated crystallisation of the precipitated yellow solid gave almost white, lath-shaped crystals of the dibromo-acid, m. p. 204° (Found: Br, 44·0. $C_{10}H_6O_3N_2Br_2$ requires Br, 44·2%).

The dibromo-acid reacts readily in alcoholic solution with hydrazine hydrate, liberating nitrogen and precipitating the hydrazide of the monohalogen acid. 0·2980 G. liberated 9·8 c.c. of nitrogen at 16° and 748 mm. One g.-mol. therefore liberates 13·9 g. of nitrogen, which corresponds with the reduction of one bromine atom.

The *hydrazide* of 3-bromo-1-phenylbarbituric acid, isolated above, forms rectangular needles, m. p. 146° (Found: Br, 25·4; N_2H_4, 10·5. $C_{10}H_{11}O_3N_4Br$ requires Br, 25·6; N_2H_4, 10·2%).

5-*Bromo*-1-*phenylbarbituric Acid.*—The calculated quantity of bromine was added to the parent acid (5 g.), suspended in chloroform (50 c.c.) and warmed on the water-bath. After ½ hour, the solution was filtered, and the solid crystallised several times from spirit, being thus obtained in faintly pink, crystalline warts, m. p. 213° (Found: Br, 28·2. $C_{10}H_7O_3N_2Br$ requires Br, 28·2%). No reduction took place on treatment with hydrazine hydrate, the above hydrazide being formed.

We (T. H. N. and D. T.) wish to acknowledge a grant from the Department of Scientific and Industrial Research which enabled us to participate in the work.

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UNIVERSITY OF DURHAM. [*Received, February 24th,* 1926.]

* It is inadvisable to use more acetic acid, as the dibromide is then not precipitated when the solution is subsequently poured on ice.

CLXII.—*The Velocities of the Reactions between Ethyl Iodide and the Sodium Salts of Various Substituted Phenols in Ethyl-alcoholic Solution.*

By LEONARD JAMES GOLDSWORTHY.

ALTHOUGH much work has been done on the relation between the constitutions of different alkyl halides and their activities towards the sodium salts of phenol and of α- and β-naphthol (Segaller, J., 1913, **103**, 1154, 1421; 1914, **105**, 106, 112; Cox, J., 1918, **113**, 666, 821; 1920, **117**, 493; Shroder and Acree, J., 1914, **105**, 2583), the effects of the substituents in the phenolic substances on the velocities have not hitherto been studied. The object of the present investigation was to ascertain the effect of introducing methyl and chlorine in different positions in the molecule of sodium phenoxide, on the rate of reaction of this substance with ethyl iodide. It was hoped that the results might be of some value in reference to the general and induced polarity effects accompanying substitution in the benzene ring.

As Segaller and others have shown, the reactions between alkyl halides and sodium phenoxides are bimolecular but of a special type, the velocity coefficients being smaller the greater the initial concentrations of the reacting substances, in accordance with the equation $k_v = k_1 + a \log v$, where v is the volume containing 1 g.-mol. of the alkyl halide and sodium phenoxide. All the reactions studied in this investigation were therefore carried out in solutions of the same strength, *viz.*, seminormal, with a view to obtain comparable results.

The following are the mean values ($k \times 10^5$) of the observed velocity coefficients for the sodium salts of the cresols and chlorophenols: Concentrations of sodium salts and of ethyl iodide, $N/2$. Temp. 42·5°.

(Phenol	702)	*p*-Chlorophenol	393
p-Cresol	918	*o*- ,,	334
m- ,,	810	*m*- ,,	278
o- ,,	726	2 : 4-Dichlorophenol	196

The results resemble those obtained by Boyd and Marle (J., 1914, **105**, 2117) in their investigation on the reactivities of substituted sodium phenoxides towards ethylene and propylene oxides, the order of the reactivities of the cresols and chlorophenols towards ethyl iodide and ethylene oxide being identical.

A possible explanation of the order of the reactivities towards ethyl iodide is suggested by the results obtained by Shroder and Acree in the study of the reactions between sodium phenoxide and

alkyl halides (J., 1914, **105**, 2582). They have shown that in a mixture of sodium phenoxide and ethyl iodide in alcoholic solution, the "ionic" and "molecular" reactions

$$Ph{\cdot}O' + C_2H_5I = Ph{\cdot}O{\cdot}C_2H_5 + I'$$

and

$$Ph{\cdot}ONa + C_2H_5I = Ph{\cdot}O{\cdot}C_2H_5 + NaI$$

occur simultaneously, the former being about five times as fast as the latter. The "ionic" reaction involves the transfer of an electron from the phenoxide ion to the iodine atom, a process which will be the more easily effected the weaker the tendency of the phenoxide ion to hold its electron—in other words, the smaller the ionisation constant of the phenol in question. We should expect, therefore, that the order of the reactivities of the phenoxides would be the inverse of the order of the ionisation constants of the corresponding phenols. The results, except in the case of sodium *o*-tolyl oxide, accord with this expectation, the ionisation constants increasing in the order *o*-, *p*-, and *m*-cresol, phenol, *p*-, *o*-, and *m*-chlorophenol, 2 : 4-dichlorophenol.* In the case of sodium *o*-tolyl oxide the retarding steric effect of the methyl group in the ortho-position may account for the unexpectedly low reactivity.

Experimental.

The ethyl alcohol used in these experiments was commercial absolute alcohol, carefully dried by digestion with lime and calcium. The ethyl iodide was purified by successive washings with dilute caustic soda solution and water, drying over calcium chloride, and distillation from silver powder. The cresols and chlorophenols, supplied by Kahlbaum, were purified by fractional distillation a few hours before use. All the instruments used were standardised against instruments carrying the certificate of the National Physical Laboratory.

The experiments were carried out at 42·5° ± 0·1° in a thermostat provided with an Ostwald toluene regulator and an efficient stirrer.

To a weighed quantity of the phenol was added a measured volume of an alcoholic solution containing an equivalent quantity of sodium ethoxide. The solution was then diluted to normal concentration by adding the calculated volume of alcohol. 50 C.c. of this solution

* The ionisation constants of phenol and the cresols have been determined by Dawson and Mountford (J., 1918, **113**, 937). The order of the constants for *p*- and *o*-chlorophenols may be deduced from the measurements of the hydrolysis of their salts by Hantzsch and Farmer (*Ber.*, 1899, **32**, 3066, 3089). It is assumed from a consideration of the induced polarity effects that the ionisation constant of *m*-chlorophenol, for which data are not available, is greater than those of *o*- and *p*-chlorophenol.

were mixed quickly with an equal volume of a normal solution of ethyl iodide, and 10 c.c. of the mixture were introduced into each of eight small test-tubes, which had been steamed out previously. The test-tubes, provided with well-fitting rubber stoppers, were then placed in the thermostat. After 10 minutes, the contents of one of the tubes were transferred quickly to a beaker containing ice and an amount of standard acid nearly sufficient to neutralise the unchanged phenoxide. The titration was completed as quickly as possible, with lacmoid as indicator. Further titrations were carried out in a similar way at suitable intervals of time. The results were calculated from the equation $k = xy/ta(a - x)$, in which y, a, and $a - x$ represent the volume (in c.c.) of acid required to neutralise the phenoxide in 10 c.c. of the mixture before the commencement of the experiment, in the first titration (zero-time), and after t minutes, respectively.

In order to economise space the detailed results of only one experiment are shown, *viz.*, that in which the salt was sodium *m*-tolyl oxide, and $N/5$-hydrochloric acid was used for titration.

t.	$a-x$.	x.	$k \times 10^5$.	t.	$a-x$.	x.	$k \times 10^5$.
0	22·15	—	—	90	13·45	8·70	811
30	18·15	4·00	829	120	12·05	10·10	788
60	15·40	6·75	824	150	10·80	11·35	791
70	14·70	7·45	817			Mean	810.

In conclusion, the author wishes to express his thanks to Mr. D. H. Peacock for the interest which he has shown in this work and for some useful suggestions.

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CLXIII.—*Carboxylated β-Diketones.*

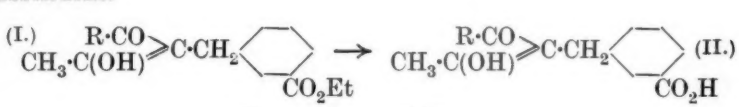
By GILBERT T. MORGAN and CHARLES RAYMOND PORTER.

IN this communication we describe the synthesis of new β-diketones containing auxiliary carboxyl groups, these substances having been prepared with the object of facilitating the resolution of metallo-β-diketones into optically active enantiomerides.

Hitherto this separation has been effected only with such salts as $[CoAc,2en]Cl_2$ and $[CoPr,2en]Cl_2$, where Ac and Pr represent the univalent radicals of acetylacetone and propionylacetone respectively (Werner, Schwyzer, and Karrer, *Helv. Chim. Acta*, 1921, **4**, 113), but not with metallo-β-diketones such as $[BePr_2]$ and $[CuPr_2]$ or $[FeAc_3]$ and $[CoAc_3]$, where the metal is wholly combined with the organic

radical. Even if the two foregoing pairs of metallo-β-diketones exist respectively in tetrahedral and octahedral forms, an experimental difficulty arises from the fact that these substances, being non-ionised inner metallic complexes, do not combine either with optically active acids or with alkaloids. Moreover, the examination of selected crystals has not in this series led to positive results.

An auxiliary acidic group has been conferred on acetylacetone by condensing the sodium salt of this β-diketone with *ethyl ω-chloro-m-toluate* (*m-carbethoxybenzyl chloride*), $CH_2Cl\cdot C_6H_4\cdot CO_2Et$, when 3-m-*carbethoxybenzylacetylacetone* (I; $R = CH_3$) was produced which by hydrolysis in concentrated sulphuric acid furnished 3-m-*carboxybenzylacetylacetone* (II; $R = CH_3$), a β-diketone containing two acidic functions, a chelate radical and the carboxyl substituent.



$R = CH_3$ or C_3H_7.

Cobaltic and chromic derivatives of the free carboxy-diketone were prepared but found to be unsuitable for resolutions with optically active alkaloids.

Homologues of the foregoing diketones with unsymmetrical chelate groups were prepared by a similar series of operations carried out on sodium butyrylacetone, when 3-m-*carbethoxybenzylbutyrylacetone* (I; $R = C_3H_7$) resulted, and this ester on hydrolysis yielded 3-m-*carboxybenzylbutyrylacetone* (II; $R = C_3H_7$).

The free carboxy-diketone (II; $R = C_3H_7$) gave a green dicupric salt convertible into a grey monocupric derivative the colour of which suggested (Morgan, Drew, and Porter, *Ber.*, 1925, **58**, 333) that the metal was held in the chelate group, but, although soluble in organic media, the monocupric compound rapidly decomposed in warm solutions into dicupric salt and carboxy-diketone.

A similar pair of beryllium derivatives was prepared, the monoberyllium compound being soluble in organic media, but crystallisation of this substance was impossible because of its rapid decomposition into ill-defined, insoluble products. Moreover, the alkaloidal salts of this monoberyllium derivative were also unsatisfactory and afforded no indication of any resolution.

Both carboxy-β-diketones exhibit keto-enol isomerism: specimens crystallised from non-hydroxylic solvents such as benzene or petroleum were more fusible and gave immediately with ferric chloride purple colorations, thus indicating the enolic variety, whereas preparations crystallised from alcohol were less fusible

and developed the coloration only gradually, thereby suggesting a diketonic modification.

EXPERIMENTAL.

Ethyl ω-*chloro*-m-*toluate* (m-*carbethoxybenzyl chloride*) was prepared by a modification of the patented method (E.P. 29720/1910; D.R.-P. 234913; Friedländer's "Fortschritte," X, p. 117). *m*-Toluic acid (100 g.) was gradually warmed to 120° with 75 c.c. of thionyl chloride and thereby converted into *m*-toluoyl chloride, b. p. 105°/20 mm. Chlorine was passed into 112·5 g. of this chloride at 160—180° until its weight increased to 138 g. The resulting ω-chloro-*m*-toluoyl chloride was warmed gently with 50 c.c. of alcohol; a vigorous reaction set in with evolution of hydrogen chloride, the flask being finally heated to 140°. The ester was washed rapidly with dilute aqueous sodium carbonate and water, dried, and distilled under reduced pressure; 130 g. (= 89%) were obtained boiling at 140—150°/12 mm. (Found: Cl, 18·4. $C_{10}H_{11}O_2Cl$ requires Cl, 17·9%).

I. 3-m-*Carbethoxybenzylacetylacetone* (I; R = CH_3).—Eighty g. of sodium acetylacetone and 130 g. of the foregoing ester were heated together under reflux at 135—145° for 3 hours and finally at 160°. The cooled product was extracted with water and ether; the dried ethereal layer was distilled, yielding acetylacetone and 84 g. of a higher fraction, b. p. 175—215°/11 mm. The less volatile fraction dissolved in alcohol and was added to aqueous copper acetate containing an equivalent proportion of ammonia. After 2 or 3 days the copper derivative was collected, and washed with dilute acetic acid to dissolve copper hydroxide and with ether to remove liquid impurities. The ethereal washings were worked up again with further distillations of crude diketone.

Copper 3-m-*carbethoxybenzylacetylacetone*, a light grey, microcrystalline powder, was insoluble in water but soluble in organic solvents; it crystallised from benzene and melted at 173—176° (Found: C, 61·3; H, 5·6. $C_{30}H_{34}O_8Cu$ requires C, 61·6; H, 5·8%).

On extraction with dilute sulphuric acid and ether 67 g. of this copper salt yielded 42 g. (= 70%) of the liquid diketone, b. p. 209—215°/12 mm., which developed a reddish-purple coloration with alcoholic ferric chloride.

Acidic Hydrolysis of 3-m-*Carbethoxybenzylacetylacetone*.—The ester was not affected by boiling with 5*N*-sulphuric acid, 40% sulphuric acid, concentrated hydrochloric acid, or glacial acetic acid. Heating with syrupy phosphoric acid led to products giving no coloration with ferric chloride.

A solution of 1 or 2 g. of the ester in 3 or 4 volumes of concentrated

sulphuric acid was heated on the water-bath; hydrolysis occurred and the cooled red liquid yielded a white solid when poured on to crushed ice. This product was crystallised from benzene or benzene–petroleum. The first mother-liquors contained unchanged carbethoxy-β-diketone, which was recovered and worked up in subsequent batches.

3-m-*Carboxybenzylacetylacetone* (II; R = CH_3), obtained by this hydrolysis in 50% yield, crystallised from alcohol in colourless needles, m. p. 130°, and from benzene in white needles, m. p. 115°. The change in melting point is reversible and is probably due to keto-enolic isomerism. A specimen crystallised from benzene gave with ferric chloride a purple coloration, whereas the preparation from alcohol developed this colour only after a time (Found: C, 67·1; H, 5·8. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%).

3-*m*-Carboxybenzylacetylacetone was fairly stable in acid solution but readily hydrolysed by alkalis (p. 1261). It was soluble in ordinary organic solvents except light petroleum and dissolved sparingly in water.

Copper Derivatives of 3-m-*Carboxybenzylacetylacetone.*—A bluish-green precipitate separated on adding excess of aqueous copper acetate to an acetone solution of 3-*m*-carboxybenzylacetylacetone. This dicupric salt containing copper attached both to carboxyl and chelate groups (Cu, 21·7. $C_{26}H_{24}O_8Cu_2$ requires Cu, 21·5%) was insoluble in the ordinary organic solvents excepting pyridine, in which it dissolved extremely readily. On concentrating the pyridine solution, a precipitate was formed which lost pyridine on drying and reverted to the original dicupric salt. This substance developed slowly a red ferric chloride coloration, decomposed to a brown paste at 250°, and lost half its copper on trituration with an equivalent proportion of *N*/10-sulphuric acid, yielding a light grey *monocupric* derivative (Cu, 11·9. $C_{26}H_{26}O_8Cu$ requires Cu, 12·0%), which decomposed at 235—240° to a brown paste. It was insoluble in all ordinary solvents, and with ferric chloride it developed a red coloration only after a few minutes. This slowness of reaction and the grey colour suggest that the copper of the monocupric salt is attached to the chelate group.

Other Metallic Derivatives.—Normal beryllium acetate added to an acetone solution of the 3-*m*-carboxybenzylacetylacetone produced a white precipitate of beryllium derivative insoluble in organic solvents. A portion of the beryllium could be removed by trituration with dilute sulphuric acid (one equivalent) and the residue was then soluble in organic media, but it could not be purified by crystallisation because it reverted to a mixture of free diketone-carboxylic acid and the diberyllium derivative of this acid.

The dark green chromium derivative, although soluble in chloroform, was transformed in the warm solution into an insoluble green vitreous mass.

II. 3-m-*Carbethoxybenzylbutyrylacetone* (I; R = C_3H_7).—Butyrylacetone prepared from methyl propyl ketone and ethyl acetate (Morgan and Drew, J., 1924, **125**, 737) was dissolved in 10 volumes of dry cold ether and converted into its sodium salt by the addition of sodium in thin slices. After collecting the separated sodium derivative, the mother-liquors were concentrated, the total yield being practically quantitative. A mixture of 110 g. of sodium butyrylacetone and 145 g. of 3-*m*-carbethoxybenzyl chloride was heated under reflux in an oil-bath. At 140—150°, the sodium salt dissolved to a clear liquid and sodium chloride separated. After an hour at 160°, the cooled product was extracted with ether and water. The ethereal layer was washed with dilute acetic acid and distilled under reduced pressure. Butyrylacetone passed over first, yielding 25 g. of its copper derivative, and a higher fraction was obtained boiling above 180°/10 mm. The less volatile portion, dissolved in alcohol, was treated with excess of aqueous copper acetate containing one equivalent proportion of ammonia. After a few days, the mixture was slightly acidified and the copper derivative collected and washed successively with light petroleum and ether. The grey copper derivative, when extracted with dilute sulphuric acid and ether, regenerated the *diketone*, b. p. 200—201°/6 mm. (yield 47 g. or 22%).

Copper 3-m-*carbethoxybenzylbutyrylacetone* was soluble in chloroform or benzene and crystallised from the latter as a light grey, microcrystalline powder, m. p. 168—170° (Found: C, 63·6; H, 6·6. $C_{34}H_{42}O_8Cu$ requires C, 63·6; H, 6·5%).

3-m-*Carboxybenzylbutyrylacetone* (II; R = C_3H_7).—The foregoing ester was hydrolysed in 1 to 2 g. lots by mixing with 3 or 4 volumes of concentrated sulphuric acid, the solution being stirred for 2 to 3 minutes on the water-bath. The cooled yellow solution was then poured on to crushed ice and the white solid crystallised as quickly as possible from carbon tetrachloride (yield 50%).

This diketonic acid was more soluble and less stable than its lower homologue from acetylacetone, the crude material being decomposed completely on boiling for more than a few minutes with solvents. It was readily soluble in these organic media and dissolved sparingly in water. When crystallised from aqueous alcohol, the diketo-acid separated in small plates sintering at 80° and melting indefinitely at 100—112°. The purple ferric coloration developed only slowly with this specimen. But a preparation crystallised from benzene–petroleum melted at 78—90° and gave

the ferric coloration immediately (Found: C, 69·1; H, 6·9. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·8%).

Copper Derivatives of 3-m-*Carboxybenzylbutyrylacetone.*—*Dicupric* 3-m-*carboxybenzylbutyrylacetone* was obtained as a bluish-green precipitate by adding copper acetate to an acetone solution of the diketo-acid. On washing with acetone, a portion dissolved and monocupric derivative was recovered from this extract. The insoluble dicupric salt decomposed to a brown paste when heated above 225° (Found: Cu, 19·4, 19·8. $C_{30}H_{32}O_8Cu_2$ requires Cu, 19·6%).

Monocupric 3-m-*carboxybenzylbutyrylacetone*, prepared as a grey powder by triturating the foregoing copper compound with *N*/10-sulphuric acid, was soluble in alcohol or acetone, but crystallisation had to be effected as rapidly as possible because the substance decomposed on boiling the solution, with formation of the free diketo-acid and dicupric compound. The monocupric compound sintered at 173° and melted to a green liquid at 176—178° (Found: Cu, 11·1. $C_{30}H_{34}O_8Cu$ requires Cu, 10·9%).

Beryllium Derivatives of 3-m-*Carboxybenzylbutyrylacetone.*—On mixing an acetone solution of 3-*m*-carboxybenzylbutyrylacetone with aqueous normal beryllium acetate a copious white precipitate was obtained insoluble in water and the ordinary organic solvents, thus corresponding in properties with the foregoing dicupric salt. This insoluble beryllium compound was triturated with a very slight excess of 2*N*-sulphuric acid, and the mixture filtered. The filtrate contained beryllium; the precipitate was now soluble in organic media. This soluble beryllium derivative could not, however, be crystallised, as its solutions in benzene or other organic solvents rapidly underwent chemical change with the formation of a gelatinous white precipitate.

Numerous attempts were made to prepare the morphine, cinchonidine, brucine, and strychnine salts of the foregoing soluble beryllium derivative, but the products were ill-defined, uncrystallisable, vitreous, or oily substances from which no definite evidence as to resolution could be deduced.

III. m-*Carboxybenzylacetone* or ω-*Acetonyl*-m-*toluic Acid*, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$.—On warming with dilute aqueous sodium hydroxide, *m*-carbethoxybenzylacetylacetone or *m*-carbethoxybenzylbutyrylacetone dissolved to a colourless solution from which acids precipitated a white solid soluble in ether. This product, which was also obtained by alkaline hydrolysis of *m*-carboxybenzylacetylacetone and *m*-carboxybenzylbutyrylacetone, was identified as m-*carboxybenzylacetone*. It was slightly soluble in water, but dissolved readily in organic media, crystallising therefrom on addition of light petroleum; it also separated from the latter

solvent in lustrous plates, m. p. 77° (Found: C, 68·5; H, 6·4. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·2%). The equivalent weight by alkalimetry was 194; theory requires 192.

IV. 3-o-*Carbethoxybenzylacetylacetone*,

$$(CH_3{\cdot}CO)_2CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2Et.$$

—*o*-Toluoyl chloride, obtained in practically quantitative yield from *o*-toluic acid and phosphorus trichloride at 120—170°, was subjected to a stream of chlorine at 160—180° without a catalyst until the calculated increase in weight had been attained. The resulting ω-chloro-*o*-toluoyl chloride boiled at 129—133°/12 mm.

When treated with a slight excess of warm alcohol, this chloride was esterified with loss of hydrogen chloride. The ethyl ω-chloro-*o*-toluate was washed with dilute aqueous sodium carbonate, dried, and distilled in small quantities, when the ester boiled at 139—143°/12 mm.

When larger quantities were distilled, after a portion of the ester had passed over, a solid product collected in the condenser which was identified as phthalide, m. p. 73° (Found: C, 71·9; H, 4·6. Calc.: C, 71·6; H, 4·5%).

Ethyl ω-chloro-*o*-toluate was condensed with sodium acetylacetone as in the case of the ω-chloro-*m*-toluate (p. 1258).

3-o-*Carbethoxybenzoylacetylacetone* was obtained by acidifying its grey *copper* derivative (m. p. 168—170°); it boiled at 196°/14 mm. and gave a reddish-purple coloration with ferric chloride (Found: C, 68·6; H, 7·1. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9%).

In the distillation of the foregoing diketone, a solid (Found: C, 73·75; H, 5·15%) of higher boiling point came over after the diketone. This product was obtained crystalline by adding petroleum to its benzene solution.

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EDGBASTON. [*Received, February 14th*, 1926.]

CLXIV.—*A Comparison of the Atomic Weights of Silicon from Different Sources.*

By PERCY LUCOCK ROBINSON and HAROLD CECIL SMITH.

RESULTS obtained in a recent redetermination of the atomic weight of boron (Briscoe and Robinson, J., 1925, **127**, 696) indicated that the value varies slightly with the source of supply. The values

10·818, 10·825, and 10·841 found for Asiatic, Tuscan, and Californian material respectively were tentatively explained as due to variation in the isotope ratio. This paper reviewed the evidence and stated the conclusion that, despite excellent work supporting the opposite contention, there was no inherent improbability in this suggestion. It is to be deplored that much of the earlier work on atomic weights has been on material of unspecified origin, as this makes the discrepancies valueless for statistical investigation. The necessity for further work on boron being obvious, the problem was attacked by comparing the densities of boric oxide from these and other sources. The results of this investigation supported the original conclusion (Briscoe, Robinson, and Stephenson, this vol., p. 70).

Late in 1924, Jaeger and Dijkstra (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 290; *Z. anorg. Chem.*, 1925, **143**, 233) showed that the densities of tetraethylsilicane indicated no difference in the atomic weight of silicon exceeding 0·019 unit, which corresponds to a density difference of 0·00010 unit—a remarkable degree of accuracy for the pyknometer method employed. The inconclusive character of these results (see Briscoe and Robinson, *Nature*, 1926, **117**, 377) led us to proceed with the redetermination of the atomic weight of silicon projected early in 1924 for the reasons given below.

A brief comparison of the geological occurrence of boron and silicon is appropriate here. Boron is widely distributed and forms about 0·001% of the earth's crust (Clarke and Washington, *Proc. Nat. Acad. Sci.*, 1922, **8**, 108). It is found primarily in tourmaline and datolite, from which it is liberated and subsequently concentrated, principally as calcium salts, by the drying up of lakes as in the Asiatic and American deposits, or artificially separated from the steam of fumaroles as at Volterra. Clearly, in each case the boron has been associated for a considerable period with the area in which it is found. Silicon, next to oxygen the most abundant element, occurs terrestrially to the extent of 25·80% (Clarke, "Data of Geochemistry," 1920, 30). The transportation of siliceous material is almost entirely by mechanical means and then only over short distances, which makes it probable that silicon has remained associated with the continental mass on which it is found for considerable geological periods. This would appear to be the case even if Wegener's displacement theory should eventually be substantiated. Thus boron and silicon, for different reasons, have probably retained for great periods of time their general relationship to that area of the earth's surface on which they are found.

Silicon presents certain well-known general chemical similarities

to boron, and, occurring as it does in three isotopic forms, Si = 28, 29, 30 (Aston, *Phil. Mag.*, 1920, **40**, 628: Si = 30; confirmed, *Nature*, 1924, **114**, 273), appears to be a suitable element for the further investigation of the constancy of atomic weight.

Determinations of the atomic weight of silicon previous to 1920, fully discussed by Clarke (*Mem. Nat. Acad. Sci.*, 1920, **16**, 22), are tabulated below (Table I) together with more recent work, under the three heads : halide : silver ratio, halide : oxide ratio, and vapour density.

TABLE I.

Halide : Silver Ratios.

Pelouze, *Compt. rend.*, 1845, **20**, 1047	28·370
Dumas, *Annalen*, 1860, **113**, 31	28·077
Schiel, *ibid.*, 1861, **120**, 94	27·945
Baxter, Weatherill, and Holmes (preliminary paper), *J. Amer. Chem. Soc.*, 1920, **42**, 1194	28·111
Baxter, Weatherill, and Scripture, *Proc. Amer. Acad. Arts Sci.*, 1923, **58**, 245	28·063, 28·061
Hönigschmid and Steinheil, *Z. anorg. Chem.*, 1924, **141**, 101...	28·105

Halide : Oxide Ratios.

Thorpe and Young, J., 1877, **51**, 576	28·381
Becker and Meyer, *Z. anorg. Chem.*, 1905, **43**, 251	28·231
Meyer, *ibid.*, 1905, **46**, 45	28·231

Vapour Density.

Jaquerod and Tourpaian, *J. Chim. phys.*, 1913, **11**, 269	28·496
Germann and Booth, *ibid.*, 1917, **21**, 81	28·306

The only values in this table which merit serious consideration from the point of view of high accuracy, as distinct from mere novelty of method, are the more recent halide : silver results. The hope that the comparatively simple and direct halide : oxide ratio might produce results of high accuracy is evidently not realised, probably on account of the difficulty of dehydrating the oxide. Reinvestigation of the method with the facilities now available might more nearly fulfil anticipations. The vapour density determinations are open to criticism on the lines suggested by Clarke (*loc. cit.*). The halide : silver ratios exhibit considerable variation, 27·945—28·370, although the four more recent values are in agreement to 1 part in 560 parts. They lie—though probably by that chemist's happy accident—on either side of Dumas's figure. There is a considerable discrepancy between Baxter's (*loc. cit.*) 1920 preliminary and 1923 final figures, *viz.*, 1 part in 550 parts. The International Committee (*J. Amer. Chem. Soc.*, 1925, **47**, 597) have given 28·06 as the rounded mean in spite of Hönigschmid's (*loc. cit.*) 28·105. Clearly, further investigation is required if the atomic

weight of silicon is to be known to a greater accuracy than about 1 part in 700 parts.

Outline of the Present Investigation.

With the element silicon the choice of a suitable compound for equivalent determination is limited to the halides, and of these the tetrachloride is certainly the most convenient. The silicates are indefinite in composition; the organic compounds, while occasionally of suitable stability and constancy of composition, are difficult to analyse with the required precision; and the oxide, into which a number of compounds may readily be converted, presents difficulties which have already been commented upon. Furthermore, the tetrachloride readily lends itself to a comparison of the atomic weights of material from different sources, provided a suitable method can be devised for the determination of its density with sufficient accuracy.

Silicon tetrachloride was prepared by chlorinating ferrosilicon, manufactured from silica, in one case from an unknown source, and in four others from known localities in Canada, the United States of America, Sweden, and France. As no British ferrosilicon of known origin was available, silicon was prepared from a Scottish pegmatite, and this was chlorinated. The sample of unknown origin was used in a purely preliminary manner to establish methods employed in the preparation, handling, and purification of the compound. About equal amounts of the five samples of known origin were prepared and they were individually subjected to a rigorous, but strictly uniform, process of purification. When pure, the density of each was determined by the use of glass floats calibrated as to density with extreme accuracy. The constancy of the molecular volume of the chlorides of the various isotopes being assumed, the apparent atomic weights were thus compared.

The Preparation of Silicon Tetrachloride.

Sources of Material.—Of the methods available for preparing silicon tetrachloride, the most convenient for producing it in quantity without using elementary silicon is that involving the chlorination of ferrosilicon, originally described by Warren (*Chem. News*, 1892, **66**, 112). Inquiries were therefore instituted into the production of ferrosilicon in various countries. The materials used were selected from samples from Europe and America, the final choice depending on the geographical locality and the geological age of the silica used in the manufacture (Table II). A British sample was thought desirable, and the pegmatite mentioned below was used as a source of elementary silicon.

TABLE II.

Europe.

(*a*) 91·2% Ferrosilicon, smelted by the Gullspangs Elektrokemiska Aktiebolag, at Gullspang, Sweden, from quartzite obtained at Anenaset, W. of Lake Animmen, Sweden.
(*b*) 75% Ferrosilicon, smelted by Keller and Leleux, at Usine de Livet, Isère, from quartzite obtained at Bourg St. Maurice, Haute Savoie, France.
(*c*) Pegmatite from a vein 4·5 miles W. of Strontian, Scotland.

America.

(*a*) 50% Ferrosilicon, smelted by the Southern Ferro Alloys Company, Chattanooga, Tenn., from silica obtained from the sandstone cap of Lookout Mountain, Alabama, U.S.A.
(*b*) 90% Ferrosilicon, smelted by the Union Carbide and Carbon Products Company, Niagara Falls, from quartzite obtained at Killarney, Ontario, Canada.

The authors wish to record their grateful thanks to these and other firms and individuals in various parts of the world who have made this investigation possible by so courteously placing material and information at their disposal.

Preparation of Silicon Tetrachloride from Ferrosilicon.—Warren's method (*loc. cit.*) was subsequently elaborated by Martin (J., 1914, **105**, 2836), but preliminary experiments showed that these complications were largely unnecessary in the present case. Chlorination of the ferrosilicon was carried out in iron tubes 3 ft. by 1·5 in. which were dried by twice heating to redness in a combustion furnace and cooling with dry air passing through them. After a run they were thoroughly washed and redried, but the majority of the tubes were perforated after two, and none lasted beyond three, chlorinations. Ferrosilicon as a coarse powder retained on a 40-mesh sieve was found to be most suitable. This was obtained by crushing the material in a Weatherhead mill; it was then dried, at 110°, in charges of 200—300 g. immediately before being put into the tubes. The iron tube was heated by a silica-tube resistance furnace. Chlorine from a cylinder was led through two sulphuric acid wash-bottles, past a T-piece manometer dipping 8 inches into frequently renewed sulphuric acid, to the reaction tube. The products were led through an adapter into a clean dry receiving bottle, cooled in a freezing mixture and fitted with an exit tube leading to a ventilator shaft. A rapid stream of chlorine was passed through the heated tube, and after 25 minutes the production of silicon tetrachloride began, and when the rate of production diminished fresh ferrosilicon was exposed to the action of the gas by rotating the tubes slightly and tapping them. Occasional slight back-pressure, due to ferric chloride, was relieved in this way, but after 2·5—3·5 hours the tubes choked up completely and thus ended the run. About 700 c.c. of crude product were obtained from each source and

hermetically sealed by closing the bottle with a tied-in waxed cork.

Preparation of Silicon Tetrachloride from Pegmatite.—The pegmatite was rich enough in silicon to be treated as an impure specimen of the oxide, and was reduced with aluminium in the presence of sulphur (Holleman, *Proc. K. Akad. Wetensch. Amsterdam*, 1904, **1**, 189; Kuhne, D.R.-P. 147871). 200 G. of finely ground mineral were very thoroughly mixed with aluminium powder (200 g.) and flowers of sulphur (250 g.), charged into a No. 6 Battersea crucible, covered with a layer of sulphur, and fired by means of magnesium ribbon set in a primer of magnesium powder and barium peroxide. Immediately following the reaction, the hot crucible was plunged into water, the aluminium sulphide being thus decomposed, leaving nodules of crystalline silicon. These were washed, dried, crushed, and finely ground in a Weatherhead mill, and this powder was treated with concentrated hydrochloric acid, when there was a marked evolution of gas and a smell suggestive of a silicide. The wash-acid was heated to boiling, cooled, diluted with water and filtered through a Buchner funnel with the aid of a pump. The resulting moist mass was digested with 1 : 2 hydrochloric acid for some time, again filtered, well washed in the funnel, and dried at 110°. 300 G. of silicon as a fine, dark grey powder were obtained from nine reductions.

About 30 g. of this material were placed in a clean dry Jena glass tube of 0·75 in. bore and chlorinated as described for ferrosilicon. The silicon glowed during the chlorination and a small quantity of white residue remained. About 700 c.c. of product were obtained and bottled as before.

Rough Fractionation of Crude Silicon Tetrachloride.—This step was introduced to rid the crude product of most of its chlorine and all its solid impurities. The cork of the bottle containing the crude material was replaced by a waxed cork, provided with a short wide delivery tube, which was already connected by means of rubber to a specially constructed fractionating column, 2 ft. long, filled with glass beads. The bottle was carefully heated by a water-bath, and a small head fraction carrying most of the chlorine was allowed to go entirely to waste. A head fraction of about 70 c.c. was now collected in a small bottle cooled in a freezing mixture and, as the last third of this fraction ran colourless, it was concluded that the bulk of the chlorine had been removed. A main fraction of about 600 c.c. was then collected in a dry litre bottle, containing 40 c.c. of pure mercury: it was stoppered as previously described. A slight flouring of the mercury in the case of each main fraction indicated that a trace of chlorine was still

present. The tail fractions subsequently yielded specimens of the hexachloride (b. p. 141·5°), and a fraction of higher boiling point that could not be driven up the column, which was, presumably, the octachloride. The amounts of higher chlorides found were less than those obtained by Martin (*loc. cit.*) in his carefully regulated chlorinations.

Purification of Silicon Tetrachloride.

The importance of a rigorous purification need hardly be stressed. The crude material possibly contained :

Chlorine	b.p. −34°	Disilicon hexachloride	b.p. 145°
Hydrochloric acid	−83	Trisilicon octachloride	212
Phosphorus trichloride	76	Antimony trichloride	226
Arsenic trichloride	130		

Silicon dioxide and its hydrates are probably only very slightly volatile in the vapour of silicon tetrachloride.

Of these compounds, only phosphorus trichloride was likely to persist, but it has a boiling point 16·5° above that of silicon tetrachloride. The methods available for purifying the liquid were fractional crystallisation and distillation, and contact with mercury and sodium. Fractional crystallisation was originally part of the scheme, but, unfortunately, became impossible by reason of the increased difficulties experienced in obtaining supplies of liquid air. The means available were thus fractional distillation and prolonged contact with liquid sodium amalgam. They were conducted in the following stages (see Fig. 1, where T, H, and M represent tail, head, and main fractions respectively) :

1. Rough fractionation through a single-column still.
2. Standing for 6 months over mercury, with frequent shakings.
3. Systematic fractional distillation in four stages, conducted in dry air at about atmospheric pressure in an all-glass four-column still.
4. Standing with frequent shakings for upwards of 2 months over sodium amalgam.
5. Fractional distillation into five fractions in a vacuum.
6. Fractional distillation into five fractions in a vacuum.

Main Fractionation of Silicon Tetrachloride at Atmospheric Pressure.—This was conducted in a 4-column still (Fig. 2) of Durosil glass similar in principle to that used in the purification of boron trichloride by Briscoe and Robinson (*loc. cit.*). Each piece of the apparatus * was cleaned with chromic-nitric acid, washed with water, rinsed with pure alcohol, and allowed to drain. The parts

* Our thanks are due to Mr. G. Ellison of this department for making the individual pieces of glass-ware used in this investigation.

were then assembled and dried by passing dry air in at M and out through T_1 for 3 days, the mercury in the valves sealing the apparatus from outside air. The capillary of the special joint was then sealed, and freshly-made sodium amalgam was filtered into M by means of a long-stemmed funnel. All exit tubes were bent to point downwards, so that any liquid condensing in the phosphorus pentoxide guard-tubes was unable to return to the apparatus.

About 600 c.c. of the roughly-fractionated crude product, after standing over mercury with repeated shaking for 5—6 months, were distilled into B_1, which was cooled in ice-cold water, leaving

FIG. 1.

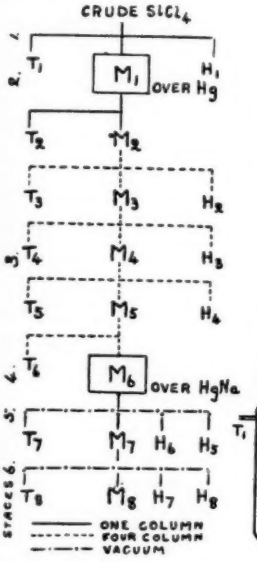
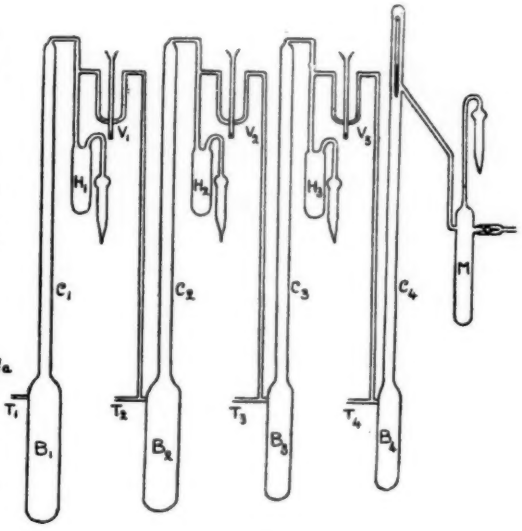


FIG. 2.



behind a tail fraction of 20 c.c. A paper jacket containing solid carbon dioxide kept the base of C_1 cool, while extra mercury which had been poured into V_1 cut off connexion between B_1 and B_2. T_1 was then sealed off. B_1 was gently warmed with a soft flame, as this method of heating gave steady boiling, and a head fraction of about 50 c.c. was distilled into H_1 which was cooled in solid carbon dioxide. This head fraction was sealed off, mercury was run from V_1 to establish connexion with B_2, and a main fraction of about 500 c.c. was distilled forward into B_2, which was cooled in iced water, the base of C_2 being jacketed with solid carbon dioxide. More mercury was poured into V_1 and the tip of T_1 was broken under rubber to connect with a phosphorus pentoxide tube, thus establishing equal pressures at both sides of the valve. A tail of

about 50 c.c. remained in B_1. Similar head and tail fractions were rejected in distillations from B_2 and B_3, resulting in 300 c.c. of material in B_4. The liquid in B_4 was then distilled forward past the thermometer into M (cooled in solid carbon dioxide) where it was sealed up. About 25 c.c. of liquid returned to B_4 on account of column capacity.

To prepare the apparatus for the next distillation the tails and drainings from the columns were distilled from the various boilers by opening the side-tubes T_1, T_2, T_3, and T_4, after which these side-tubes were sealed up and dry air was passed completely through the apparatus for 3 or 4 days with occasional warmings, thus removing the last traces of silicon tetrachloride: the new head-bulbs were then fused on, and the apparatus carefully dried for the next sample.

The Boiling Point of Silicon Tetrachloride.—This is a useful criterion of purity, and it was measured with all the accuracy possible under the conditions of the experiment. The thermometer used (range 10—60°) was subsequently compared with the N. P. L. thermometer mentioned below, and was usually less than 0·02° in error. Temperatures, which remained fairly steady, were taken at short intervals, any fluctuations being traceable to variations in the rate of distillation which caused slight pressure changes in the system. There was absolutely no tendency towards a rise of temperature during the last stages of each distillation. Table III gives the mean boiling point and atmospheric pressure for each sample.

TABLE III.

Sweden	57·10°	761·6 mm.	France.....	56·83°	753·9 mm.
Scotland	56·95	758·0 mm.	Canada	56·91	756·0 mm.
U.S.A.	57·12	763·3 mm.			

This indicates a boiling point between 57·02° and 57·05° at 760 mm., a figure in fair agreement with the 56·9° of Becker and Meyer (*loc. cit.*) and the 56·8° of Stock, Somieski, and Wintgen (*Ber.*, 1917, **50**, 1754).

[*Special Note on the French Fraction.*—A few days after distillation the vessel containing the main fraction of the French material from the 4-column still developed an extensive series of cracks round the upper portion near the special joint. Since there was no apparent entry of air into the container, it was painted over with thick collodion varnish, bound with pure rubber tape and finally painted with a viscous solution of pure rubber. After standing for some days, it was joined to a new, clean, dry special-joint container provided with fresh sodium amalgam, the strains between the two vessels being relieved by a number of right-angle

bends in the thin-walled connecting tube. The special joint was then broken, and, with the exception of about 10 c.c., the liquid was poured into the new vessel, the exit tube of which carried a phosphorus pentoxide guard-tube.]

First Vacuum Distillation of Main Fractions.—The containers, holding the five main fractions from the 4-column still, were severally sealed to trains (Fig. 3) consisting of a small head-bulb A and

FIG. 3.

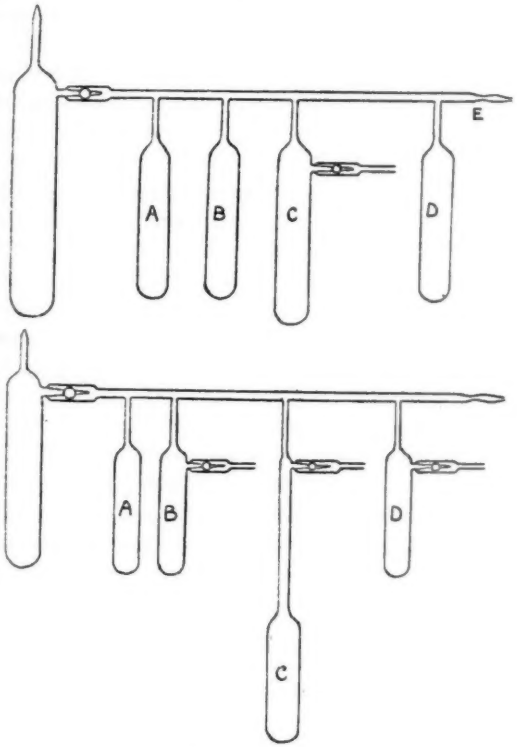
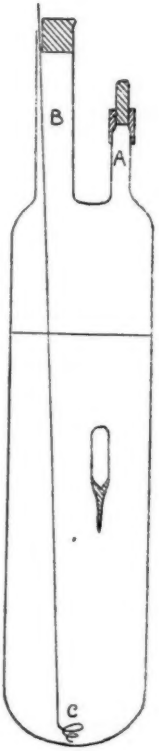


FIG. 4.

FIG. 5.



containers, B for the head fraction proper, C provided with a special joint for the main fraction, and D for the tail fraction. The train was evacuated five times while at about 120°, being each time slowly filled with dry air, and finally allowed to cool under atmospheric pressure. The silicon tetrachloride was cooled with liquid air to near its freezing point, and the capillary of the special joint was broken with the train at atmospheric pressure though still protected from moisture by the drying train. It was evacuated

and sealed off at E when the manometer registered less than 2 mm. pressure. (In the course of these distillations it was observed that solid silicon tetrachloride at very low pressures retained permanent gas which was disengaged when the solid melted.) A small head fraction of about 10 c.c. was collected in A which was sealed off, and a head fraction of 50 c.c. was distilled into B. A main fraction of about 150 c.c. was collected in C and a tail of about 50 c.c. in D, the amalgam in the original container being left quite dry.

The " hammer " of silicon tetrachloride in a vacuum at temperatures near its freezing point was considerable enough to render cautious handling absolutely necessary.

Second Vacuum Distillation of Main Fractions.—This was carried out after fusing to the train the main fraction containers obtained above (Fig. 4). The material was now so pure that head and tail fractions were worth preserving, and thus B and D, in addition to C, had special joints. C was specially constructed with a long neck so that it could be introduced into a water-bath, and before fusing on, into it were placed the two floats to be used subsequently in determining the density of the liquid. Very special precautions were taken in the washing and drying of the whole apparatus before the final evacuation: before the various parts were actually fitted together, each piece was treated with chromic–nitric acid for about 12 hours, well washed with tap water, then with ordinary distilled water, and finally with pure alcohol and ether and left to dry. On the day before assembling, each piece was treated with four large washings of special distilled water, followed by two with pure dry alcohol and two with pure ether. In assembling, the vessels which had to be sealed off during the course of the fractionation were held by clamps lined with asbestos paper—a provision which entirely prevented the sticking of cork and glass by repeated heating.

Each complete train was tested on the pump, and any minute leaks, which occasionally occur in such a high-melting glass as Durosil, were fused up. When finished, the apparatus was heated to about 120°, twice evacuated and slowly filled with dry air, and allowed to stand overnight protected by a new phosphorus pentoxide guard-tube. It was then evacuated six times with heating and slow refilling with dry air, the final evacuation, lasting 30 minutes, being made with the whole of the glass as near 200° as possible, and the manometer recording zero pressure when the apparatus was sealed off from the pump.

In distilling, the procedure was first to cool the whole of A with liquid air, at the same time heating C to 120°, and thus to remove any moisture from the surface of C and deposit it in A. With

these conditions still obtaining, the special joint was broken, and *instantly* a snow of solid silicon tetrachloride covered the surface of A, thus fixing any moisture and retaining it in that part of the apparatus. Further cooling was at once applied, and in about 5 minutes a small head fraction (6—9 c.c.), most of the residual air, and probably all the products of hydrolysis, if any, were removed from the system by sealing off A. This was followed by a head of about 30 c.c. in B, a main of about 60 c.c. in C, and a tail fraction of about 30 c.c. in D, leaving the original vessel dry and with the merest trace of white residue, which was greatest in the French and least in the Scottish sample. During the distillations into A and B the container C was kept warm, and the greater part of most of the distillations took place at below 0° as shown by a coating of ice on the outside of the vessels.

Before introducing them into C, the floats were gently polished with clean, well-washed linen, and a careful record was made of the destination of each float.

The Preparation and Standardisation of the Floats.

Since no method of density determination which involved exposure to air could be used with silicon tetrachloride, recourse was had to the use of glass floats. This method appeared likely to give results of much greater comparative accuracy than the older means, and actually proved to do so. It involved the preparation of two sets of floats with densities slightly above and slightly below the density of the liquid at the proposed temperature of the measurement; the determination of the relative density of these to the highest degree of accuracy attainable; and finally the observation of the flotation-temperature of pairs of these floats in the various specimens of liquid under examination. Thus, at these two temperatures the density of the liquid was known, and could be calculated very accurately at an intermediate temperature provided the interval was small. The use of two floats gave the necessary information as to the coefficient of thermal expansion of the liquid.

Construction of Floats.—Floats were made from thin-walled Durosil glass tubing of about 3 mm. external diameter and were of the form shown in Fig. 5. The barrel was about 12—15 mm. long, and the solid tail, which was about the same length, was in the form of a long taper. The finished floats had a smooth surface without any indentations which might serve as a place of lodgment for small bubbles. Large numbers were made and those for final adjustment were chosen by elimination. The final adjustment of the two sets was made using bromobenzene at constant temperatures

of 22·5° and 29·5°, respectively, and small amounts of glass were added to, or removed from the tails of the floats until their densities very closely approximated to that of the liquid at one of these temperatures. The magnitude of this apparently simple task will be recognised when it is remembered that 1·0° difference in flotation temperature is equivalent to about 0·001 density unit.

These bromobenzene temperatures had been chosen after comparing the flotation-temperatures of three floats in fairly pure silicon tetrachloride and then in the bromobenzene.

Determination of the Density of the Floats.—The density of the floats was determined by ascertaining very precisely the flotation-temperature of each float in a liquid, the density of which was afterwards determined at that particular temperature. It was realised that for the present purpose high accuracy in relative density was more important than the absolute value.

The ideal flotation-liquid would be a pure substance stable in air, non-hygroscopic, of comparatively high boiling point and having a density and a coefficient of thermal expansion about those of silicon tetrachloride. Bromobenzene approaches this ideal very closely; its density is 1·494 at 20° (Young, *Journ. de Phys.*, 1909; Perkin, J., 1896, **69**, 1202); its coefficient of expansion is very near that of silicon tetrachloride, 1° change in temperature altering the densities to the extent of 0·0010 and 0·0011 unit, respectively, and its boiling point is 156° (Young, *loc. cit.*). The material first used was as supplied by The British Drug Houses, Ltd., since absolute purity seemed to be immaterial, but after it had been in use for some days a redetermination of the flotation-temperatures of three floats indicated that the liquid was changing in density (see Table IV). The liquid was therefore redistilled with the

TABLE IV.

Float.	1st Flotation-temp.*	2nd Flotation-temp.*	Difference.
C	20·735° (Oct. 30th)	20·765° (Nov. 4th)	0·030°
D	20·635 ,,	20·650 ,,	0·015
H	20·730 (Nov. 2nd)	20·758 ,,	0·028

* Not corrected for exposed stem.

rejection of considerable head and tail fractions. The main fraction gave a very constant boiling point (155·4°/754·1 mm.), and if the distillate was not now chemically pure, it was at least composed of substances not readily separated by the conditions obtaining during the flotation tests. The distilled liquid was exposed to the atmosphere for 7 days, being adequately protected from dust, in order to acquire a normal moisture content. A redetermination

of the flotation-temperatures of Floats C, D, and H indicated that the density of the liquid had changed considerably (Table V).

TABLE V.

Float.	2nd Flotation-temp.*	3rd Flotation-temp.*	Difference.
C	20·765°	25·856°	5·091°
D	20·650	25·736	5·086
H	20·758	25·838	5·080

* Not corrected for exposed stem.

On November 12th and 13th a complete set of flotation-temperatures was obtained, this being followed by the determination of the density of the liquid, and between November 17th and 20th another complete set was added. The second set showed a fall, varying between 0·007° and 0·020°, increasing with the passage of time throughout the 3 days, indicating a fall in density of the liquid which was attributed to the further absorption of moisture from the atmosphere.

The flotation-vessel was of Durosil glass in the form shown in Fig. 5, the body being about 3·5 cm. by 16 cm., and was about three-quarters filled with liquid. A was a narrow tube normally closed by a rubber cap, while B was a wider opening through which the floats were introduced and removed, and which was closed by a small cork with a groove for the passage of the float-lifter, C. This was made of No. 19 S.W.G. nichrome wire carefully cleaned and polished, and appeared to suffer no attack by the liquid. The spiral at the end served to hold the floats in a vertical position during their passage through B. The floats were handled carefully by means of nickel-plated forceps and were polished by clean, well-washed linen on entering and leaving the liquid. The wire was not lifted farther out of the liquid than was absolutely necessary and was allowed to fall back into its place after use; and, except when changing floats, B was corked and protected from dust by an inverted test-tube D. Thus every endeavour was made to ensure the permanence of the liquid during the period of the flotation-tests.

The temperature of the flotation-liquid was regulated by submerging the vessel in a tank of square cross-section holding about 27 litres of water and having large plate-glass windows at the front and back. The bath was provided with a large, mechanically-driven, propeller-shaped stirrer, an electric heater consisting of a nichrome element inside a vitreosil tube, and a cooling coil consisting of several turns of $\frac{3}{8}$-inch "compo" gas-piping connected to the ordinary water supply which, at the particular season of the year in question, was cold enough.

The thermometers used were: (*a*) Thermometer 1—a special open-scale thermometer reading from + 9·5° to + 25°, graduated in 0·02° and easily read to 0·005°; (*b*) Beckmann I; (*c*) Beckmann II. In use, the bulb of each thermometer was about 8 inches below the surface of the water and the portion remaining was surrounded by a jacket containing water in which was a second ordinary thermometer giving the stem temperature. The observed temperature was corrected by means of the usual formula $s = an(T - t)$ with $a =$ 0·000143 (Thorpe, J., 1880, **37**, 160). Thermometers (*a*) and (*b*) were set in definite relationship, the permanence of the setting being tested from time to time, and, finally, each of the three thermometers was carefully compared with a 0°—50° open-scale thermometer, graduated in 0·02°, and recently calibrated at the National Physical Laboratory to 0·01° at each degree. All temperatures were thus accurately converted from the various arbitrary scales into degrees Centigrade.

Two methods suggested themselves for the purpose of obtaining flotation-temperatures: (*a*) by maintaining such a temperature that the float remained balanced in the liquid for a considerable period, say 20—30 minutes; (*b*) by making such slight variations in temperature as would cause the floats to rise or fall, and to take the mean of the last closely-agreeing pair of readings as the flotation-temperature. As some of the temperatures were 15° above that of the air in the room, the static method presented considerable difficulties in maintaining a constant temperature and, furthermore, failed to disclose any lag between flotation-liquid and bath temperatures. The second method was, therefore, adopted and was later modified by taking the mean of a number of *rise* and *fall* temperatures, and, by a series of time–temperature readings, ascertaining the rate at which the temperature of the bath varied. No useful purpose would be served in giving in detail all the readings from which the flotation-temperatures were ultimately derived, but a general idea of the accuracy may be obtained from the fact that out of 40 flotation-temperatures, 6 were derived from values 0·005° apart, 24 from values 0·010° apart, and 9 from values 0·015° apart.

The density of the flotation-liquid (bromobenzene) was determined at 25·655°, 25·666°, 33·213°, and 33·210°, the same pyknometers and method of filling being used as already described in a recent publication (Briscoe, Robinson, and Stephenson, *loc. cit.*), and only the special precautions taken to secure accuracy need be mentioned here. The pyknometer was weighed against a tare with calibrated weights on a No. 7 S.W. Oertling balance with a sensitivity of 21 divisions per mg. The vacuum weight of the

pyknometer was calculated from three separate weighings before, during, and at the conclusion of the determination, and its absolute volume was obtained by duplicate water-fillings at the two temperatures and the use of the value for the specific volume of water (Kaye and Laby, " Physical and Chemical Constants," 1911, p. 22). The liquids were delivered into the pyknometer at as near the correct temperature as possible; then the vessel was held in the bath at about 0·10° below the required temperature for upwards of 30 minutes, after which heat was gently applied and the temperature maintained for about 5 minutes at 0·01° below and then finally raised to the required temperature. In order to eliminate both speculation and observational error the temperature at the latest stage was taken at half-minute intervals and when it had remained fixed for about 4 minutes the setting was made. These temperatures were probably less than $\pm$ 0·001° in error and their accuracy was far beyond that justified by the precision of the pyknometer setting. The densities (g. per c.c.) of the flotation liquid are in Table VI, where some corresponding values by Perkin (J., 1896, **69**, 1202) are given for comparison.

TABLE VI.

t.	*d*.	*d* (Perkin).	
25·665°	1·48766	25°/25°	1·4886
33·210	1·47741	30 /30	1·4841
		35 /35	1·4798

The flotation-temperatures (corrected for exposed stem) determined before and after the density work are in columns 2 and 3 respectively of Table VII, while in column 4 are the absolute flotation-temperatures derived from column 2 by the application of the calibration correction. The densities of the floats (in g. per c.c.) calculated by assuming a straight-line relationship between density and temperature over the 7·6° range are in column 5.

TABLE VII.

Float.	2nd Flotation-temp.	3rd Flotation-temp.	Absolute Flotation-temp.	*d*.
D	25·751°	25·736°	25·746°	1·487550
A	25·855	25·848	25·850	1·487407
E	25·849	25·841	25·844	1·487416
H	25·851	25·838	25·846	1·487413
C	25·866	25·858	25·861	1·487393
Q	32·933	32·915	32·950	1·477734
M	32·943	32·933	32·960	1·477721
L	33·013	33·003	33·028	1·477628
K	33·063	33·043	33·082	1·477554
I	33·073	33·048	33·092	1·477541
				x x* 2

The Density of the Five Samples of Pure Silicon Tetrachloride at 20°.

The flotation-temperatures of the two floats in the various samples gave data for the calculation of the densities of the liquids at 20·000° and their coefficients of expansion over the range 17·1° to 21·7°. In this case again a straight-line relationship was assumed over the 4·6° range.

The peculiar behaviour of the floats in silicon tetrachloride calls for comment, if for no other reason, because of the trouble it gave. The main fractions were removed from the fractionating train almost entirely in the solid condition; on the solid melting, the released floats came to the surface, and when the liquid attained room temperature (18—20°) one in each case went slowly to the bottom : in brief, the floats moved quite normally in the liquid, but with a greater velocity than in the bromobenzene for an equal temperature change on account of difference in viscosity. It was found, however, that movement of the liquid in the vessel, by shaking or even by the tremor set up by a small motor running on the same bench, caused each float to assume a positive electrical charge. These charges have not yet been completely investigated, but they were sufficient at the time to cause the floats to stick so firmly to the side of the vessel that only the most violent shaking could dislodge them, and then only for the moment, for, once released, they immediately stuck fast elsewhere. The charges gradually decreased in magnitude with the passage of time, but they were easily acquired again and evidence up to the present appears to indicate that they are not lost completely after a period of several weeks, though they may be so small as not to affect the movement of the floats.

The Flotation-Temperatures in Silicon Tetrachloride.—To avoid any tremor in the liquid the water-bath was fitted up in a room reserved for the purpose : the permanent, wall-side bench carried the bath, with stirrer, etc., while in front of this bench, but not touching it, was a small, absolutely steady, heavy table on which was the retort-stand carrying the container, the body of which was submerged 1·5 to 2 inches below the surface of the water. It was found that when the floats had very little charge they left the side or bottom with extreme readiness when the density was reached, and that once in the centre they could be made to go up and down several times without touching the side, surface, or bottom. When the charge was slightly greater, the floats could be dislodged by giving the retort-stand a smart tap, and when once moving even these floats could be made to go up and down several times before attaching themselves to the sides again. When the behaviour of the floats was worse than this, the container was

removed from the bath and allowed to stand for several days without disturbance. In all, 105 rising and falling temperatures were taken on the ten floats, and concordant repetitions had to be obtained before the values were accepted, but this checking, whilst it ensured absolute satisfaction, was in reality hardly necessary, for, invariably, once a float was moving freely it gave concordant results, whereas the presence of a charge too great to allow of proper freedom was immediately evident. It is probable that these flotation-temperatures in spite of the above difficulty were, by reason of increased experience and the reduced viscosity of the liquid, more accurate than the earlier ones taken in bromobenzene. Table VIII gives these flotation-temperatures in respect of each float, the corresponding density of the liquid at that temperature, and the calculated density at 20·000°.

TABLE VIII.

Source.	Float.	Flotation-temp.	d at flotation-temp.	d at 20°.
Canada	E	17·044°	1·487416	1·481231
	K	21·757	1·477554	
U.S.A.	D	16·969	1·487550	1·481230
	M	21·683	1·477721	
Sweden	C	17·046	1·487393	1·481223
	I	21·763	1·477541	
Scotland	H	17·046	1·487413	1·481266
	L	21·748	1·477628	
France	A	17·062	1·487407	1·481273
	Q	21·695	1·477734	

Discussion of Results.

The Densities.—The densities of silicon tetrachloride above have an extreme variation of 0·000050, and have a mean value of 1·481245. A careful review of the method leads to the belief that these densities have a relative accuracy greater than $\pm$ 0·000005, but their absolute value is more difficult to assess because it is based on the densities of bromobenzene, and these may possibly deviate as much as $\pm$ 0·0002 from the truth but probably not more than this. Unless the errors in the densities of bromobenzene at the upper and lower temperatures respectively are both in the same direction, their effect will be reduced in the process of computation and the absolute density of the floats is likely to be less than $\pm$ 0·0002 in error, whilst in the same way the calculation used to arrive at the density of the silicon tetrachloride probably further diminishes the error here. Thus the density of silicon tetrachloride under the pressure of its own vapour (*i.e.*, 21 mm., Becker and Meyer, *loc. cit.*; Regnault, *Mem. Acad.*, 1826, **26**, 476) at 20·000° $\pm$ 0·0005° is 1·481245 $\pm$ 0·00005. This figure bears little

relationship to the previous results given below, and the reasonable presumption is that the material used by these workers was of doubtful purity.

Koster, *Jahresber.*, 1826, **6**, 120	1·54
Pierre, *Ann. Chim. Phys.*, 1847, **20**, 27	1·52371 at 0°
Mendeléeff, *Compt. rend.*, 1860, **51**, 96	1·4928 at 15°
Friedel and Crafts, *Ann. Chim. Phys.*, 1866, **9**, 5	1·522
Haagen, *Pogg. Ann.*, 1867, **131**, 122	1·4878 at 20°
Thorpe, *Ber.*, 1876, **9**, 509	1·52408 at 4°
Abati, *Gazzetta*, 1897, **27**, 437	1·47556 at 22°
Stiefelhagen, *Dispersion Flüssiger Trichloride und Tetrachloride für ultraviolette Strahlen*, Berlin, 1905	1·524 at 16°
Ruff and Albert, *Ber.*, 1905, **38**, 53, 2222	1·4933 at 15°

The Coefficients of Thermal Expansion.—The figures given in Table VIII may obviously be used to calculate the coefficient of thermal expansion of the liquid. There seems to be no *a priori* reason for supposing that a slight difference in the isotope ratio should have any effect on this physical constant; furthermore, this constant is in a measure independent of the density determination, depending as it does upon the temperature interval only and not upon the actual readings giving the interval, and it should therefore afford an excellent check upon the soundness of the method. These coefficients of thermal expansion are given in Table IX, in which, for ease of comparison, the densities also are recorded. The former have an extreme variation of 0·0000080, and a mean value of

TABLE IX.

Source.	Density.	Diff. from mean.	Coeff. of expansion.	Diff. from mean.
Canada	1·481231	−0·000014	0·0014163	+0·0000039
U.S.A.	1·481230	−0·000015	0·0014109	−0·0000015
Sweden	1·481223	−0·000022	0·0014136	+0·0000012
Scotland	1·481266	+0·000021	0·0014083	−0·0000041
France	1·481273	+0·000028	0·0014129	+0·0000005
Mean	1·481245	±0·000020	0·0014124	±0·0000022

0·0014124, which has an error probably less than ± 0·0000022. This figure is decidedly lower than the previous determinations, 0·001430, due to Pierre (*Ann. Chim. Phys.*, 1851, **33**, 241), and 0·001446, due to Thorpe (*Proc. Roy. Soc.*, 1876, **24**, 283). Without criticising the methods of the earlier workers, it will suffice to examine briefly the basis of the present determinations, *viz.*, the density and temperature intervals. The density interval depends on the densities of bromobenzene at the two temperatures: the greater the density difference the greater the coefficient of expansion indicated. Reference to p. 1277 will show that the difference in density for the given interval of temperature, 7·545°, is 0·01025 unit, whilst Perkin (*loc. cit.*) found for 10° a difference of only

0·0088 unit. Thus if Perkin's densities had been used the resulting coefficients would have been still lower. Enough has been said about flotation-temperatures to make it clear that considerable confidence may be placed in results based on them. The concordance shown by the results lends additional weight to the suggestion that they should be accepted with complete rejection of the previous data.

As criteria of the accuracy of the densities it is important to note that considerable departure from the mean seems to alternate between density and expansion in each case except in the sample from Scotland. The sample from Sweden shows the best figures. The table indicates that the causes producing the deviations are acting fortuitously, and that the errors are evenly and accidentally distributed. Thus a consideration of either column increases confidence in the other.

The Relative Atomic Weights.—Taking 1·481245, the mean density of the various samples, as equivalent to Si = 28·060, the atomic weights corresponding to the various densities found are set out in Table X.

TABLE X.

Origin.	Density.	At. wt.	Origin.	Density.	At. wt.
Canada	1·481231	28·059	Scotland	1·481266	28·062
U.S.A.	1·481230	28·059	France	1·481273	28·063
Sweden	1·481223	28·058	*Mean*	1·481245	28·060

Assuming the relative accuracy of the densities given above, these are capable of indicating changes in the atomic weight of the order of 0·001 unit, and it may reasonably be asked whether they are actually doing so here. The high value found for the French sample may perhaps be explained by the cracking of the container (see p. 1270)—a view which gains support from the observation subsequently made (see p. 1273) that this sample yielded the greatest trace of residue in the second vacuum distillation. Nothing is known against the sample from Scotland, but the considerable deviation of the coefficient of thermal expansion from the mean is probably not without significance. The evidence indicates that no greater variation than 0·005 unit in the atomic weight is to be expected in the samples of silicon under consideration.

The Use of Floats Generally.—It has been shown that carefully calibrated floats are capable of giving densities of liquids to a very high degree of accuracy, but it is also clear that the method could be greatly refined now that a knowledge of the technique has been obtained. To just what limit the method could be extended is not yet known. It has the advantage, however, of being applicable to any liquid which does not attack glass or silica, and may

be used to determine the coefficients of expansion and compressibility, and to follow the changes in liquids undergoing treatment in closed vessels.

The authors wish to express their deep indebtedness to Professor Briscoe for the facilities he has afforded and the interest he has constantly taken in this investigation; and they desire to acknowledge a grant from the Department of Scientific and Industrial Research which has enabled one of them (H. C. S.) to take part in this work. They have also to thank Capt. F. P. Mills, of the Northumberland and Durham Rescue Brigade, for kindly supplying the necessary liquid air.

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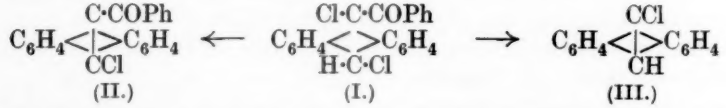
CLXV.—*The Reactivity of* meso-*Substituted Anthracenes. Part I.*

By JAMES WILFRED COOK.

It has already been shown (Barnett, Cook, and Grainger, J., 1922, **121**, 2060; Barnett, Cook, and Matthews, J., 1923, **123**, 1997; Barnett and Cook, J., 1923, **123**, 2631; 1924, **125**, 1084; Barnett, J., 1925, **127**, 2040) that in many cases *meso*-substituents in the anthracene ring system render compounds formed by addition to the " bridge " unstable or incapable of existence. The investigation of 9-benzoylanthracene (anthraphenone) has now shown that the presence of the benzoyl group hinders the formation of additive compounds. Thus with bromine no additive compound could be obtained, the sole product being 10-bromoanthraphenone. With chlorine, a similar result was obtained, although in one instance an additive compound (I) was isolated which, slowly at the ordinary temperature and rapidly on heating, lost both hydrogen chloride and benzoyl chloride and passed into a mixture of 10-chloroanthraphenone (II) and 9-chloroanthracene (III):

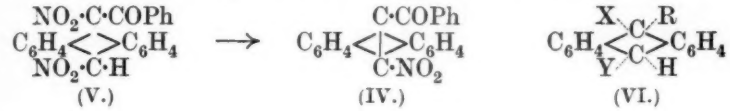


(II.) (I.) (III.)

This behaviour suggests that the additive compound had the *trans*-configuration, but unfortunately all attempts to repeat the preparation failed, the sole product being 10-chloroanthraphenone.

The action of nitric acid on anthraphenone leads to 10-nitro-

anthraphenone (IV) (compare Lippmann and Keppich, *Ber.*, 1900, **33**, 3086), no additive compound being isolated, but with nitrogen dioxide addition takes place easily and leads to a moderately stable dinitro-compound (V) which readily loses nitrous acid under the influence of cold pyridine and passes into 10-nitroanthraphenone :



(V.) (IV.) (VI.)

The " negative " or unsaturated benzoyl group thus resembles other negative groups in its ability to render *meso*-additive compounds unstable, and this behaviour is in general harmony with the idea of valency developed by Werner. Thus an unsaturated group at position 9 will appropriate some of the free affinity of that carbon atom ; the carbon atom at 10 will accordingly have relatively more free affinity, encouraging substitution by addition at 10 rather than by addition to the " bridge." In derivatives of 9 : 10-dihydroanthracene (VI) the union of each *meso*-carbon atom with two unsaturated benzene nuclei results in a comparatively small amount of affinity being available for holding the other groups. These groups are thus endowed with considerable free affinity and are consequently very reactive. Thus, direct bromination of dihydroanthracene takes place with great ease, and in anthracene dibromide (R = H ; X = Y = Br) the bromine atoms are very much more reactive than in a simple aliphatic bromo-compound. The tenacity with which X is held should be decreased by increasing the unsaturated nature of R, since unsaturation in R will lead to this group appropriating more affinity and hence leaving less available for holding X. A phenyl group is more unsaturated in nature than a benzoyl group (Werner, *Ber.*, 1906, **39**, 1278), so that phenylanthracene should give less stable additive compounds than benzoylanthracene. This is in accordance with fact, since, as already stated, benzoylanthracene gives an additive compound with nitrogen dioxide, whereas phenylanthracene does not (Barnett, *loc. cit.*). On the basis of the above argument the more saturated benzylanthracene should show greater capacity for undergoing additive reactions and should yield more stable additive compounds. That this is the case will be shown in a future communication.

The nature of the group R is not, of course, the only factor which influences the stability of these additive compounds. The influence of their geometrical configuration has been shown in the case of the two stereoisomeric 1 : 5-dichloro-9 : 10-dihydroanthraquinols (Barnett, Cook, and Matthews, *Rec. trav. chim.*, 1925, **44**, 729) and

the ease with which re-establishment of the " bridge " takes place must also be affected by the affinity which the groups at 9 have for the groups at position 10.

The acyl group in the *meso*-ketones of the anthracene series is less firmly held than is usually the case with aromatic ketones. Thus anthraphenone and its chloro- and bromo-derivatives are completely hydrolysed by brief boiling with sulphuric acid in acetic acid (compare Krollpfeiffer, *Ber.*, 1923, **56**, 2360) and anthroylbenzoic acid exhibits similar instability (Heller, *ibid.*, 1921, **54**, 3627). It has already been shown (Barnett, Cook, and Matthews, *loc. cit.*) that the facile hydrolysis of anthranyl ethers is due to primary addition to the " bridge," and the hydrolysis of the ketones may be due to a similar cause, but rigorous proof is lacking. The fact that hydrogen bromide is liberated during the hydrolysis of bromoanthraphenone cannot be cited as an argument, as 9-bromoanthracene behaves in the same way under similar experimental conditions. This view of the mechanism receives support from the observation that 10-nitroanthraphenone, 10-benzoylanthraphenone and 9 : 10-dihydroanthraphenone are not hydrolysed by boiling with sulphuric acid in acetic acid. In the first two cases the attachment of an unsaturated group at position 10 may be regarded as diminishing the free affinity of this carbon atom and thus inhibiting 9 : 10-addition. In the last case addition of this nature is not possible.

Neither anthraphenone nor any of its derivatives shows any signs of visible fluorescence, so that the carbonyl group is presumably a powerful bathoflore.

Experimental.

Anthraphenone.—The condensation of anthracene with benzoyl chloride in presence of aluminium chloride or zinc dust (Perrier, *Ber.*, 1900, **33**, 816; Lippmann and his co-workers, *ibid.*, 1899, **32**, 2249; 1900, **33**, 3086; 1901, **34**, 2766; Krollpfeiffer, *loc. cit.*) is troublesome to carry out and tarry by-products are formed. Benzoic anhydride was therefore substituted for benzoyl chloride (compare Noller and Adams, *J. Amer. Chem. Soc.*, 1924, **46**, 1889).

To a suspension of finely ground anthracene (90 g.) in carbon disulphide (750 c.c.) was added powdered anhydrous aluminium chloride (150 g.), followed by benzoic anhydride (175 g.*). Reaction took place with liberation of hydrogen chloride and was brought to completion by 4 hours' heating on the water-bath.

* If only one molecule of benzoic anhydride is employed there is formed the eutectic mixture of anthraphenone and anthracene, m. p. 158°, described by Lippmann and Keppich (*loc. cit.*) and the anthracene cannot be removed by any simple treatment.

The dark aluminium compound was decomposed with water and hydrochloric acid, the carbon disulphide removed by steam distillation, and the benzoic acid extracted from the residue by treatment with sodium hydroxide solution. After drying, the brown reaction product was treated with boiling glacial acetic acid (750 c.c.). The filtered solution, on cooling, deposited crystals which, recrystallised from benzene and then from acetic acid, yielded 85 g. of pure anthraphenone, m. p. 148°. This developed a fugitive, pure blue coloration in sulphuric acid.

The residue insoluble in acetic acid was recrystallised twice from nitrobenzene (yield, 15 g.), then from pyridine and alcohol, and finally from xylene. It formed a cream-coloured, crystalline powder, m. p. 320°, and gave a purplish-red solution in sulphuric acid (Found: C, 87·0; H, 4·8; *M*, in naphthalene, 401. Calc. for 9 : 10-dibenzoylanthracene: C, 87·0; H, 4·7%; *M*, 386). Lippmann and Fleissner (*Ber.*, 1899, **32**, 2249) obtained this substance as a by-product in the preparation of anthraphenone, but in a later paper (Lippmann and Keppich, *ibid.*, 1900, **33**, 3086) the by-product was described as tribenzoylanthracene. This compound gave anthraquinone on oxidation and this and other properties of the substance indicate that it was really impure dibenzoylanthracene.

9 : 10-Dibenzoylanthracene is obtained in 20% yield when anthraphenone is treated with an excess of benzoic anhydride in presence of anhydrous aluminium chloride. The positions assigned to the benzoyl groups follow from a study of the reduction products (future communication).

10-*Bromoanthraphenone*.—A suspension of anthraphenone (2·5 g.) in carbon disulphide (15 c.c.) was cooled in a freezing mixture, and bromine (0·5 c.c.; 1 mol.), dissolved in carbon disulphide (5 c.c.), was added slowly. Hydrogen bromide was liberated and since the addition of pyridine yielded only pyridine hydrobromide and no quaternary salt it is unlikely that addition of bromine had occurred. The bromo-derivative was obtained by evaporating the solution and crystallising the residue from acetic acid, benzene, and finally ethyl acetate (Found: Br, 22·0. $C_{21}H_{13}OBr$ requires Br, 22·2%).

10-*Bromoanthraphenone* forms pale yellow nodules, m. p. 175—176°. It gives a deep blue solution in sulphuric acid, the colour being less fugitive than in the case of anthraphenone itself. The same compound is obtained when the bromination is carried out in boiling glacial acetic acid solution. If two molecules of bromine are employed and the boiling is continued for an hour, the bromoanthraphenone is contaminated with 9 : 10-dibromoanthracene, this compound being formed by partial hydrolysis of the bromoanthraphenone and subsequent bromination.

10-*Chloroanthraphenone*.—Anthraphenone (5·6 g.) was added to a solution of chlorine in carbon tetrachloride (20 c.c.; 7·5%, wt.-vol.), the mixture boiled for 15 minutes, cooled, and light petroleum added. The resulting solid crystallised from glacial acetic acid, benzene and finally ethyl acetate in yellow nodules, m. p. 164—165° (Found : Cl, 11·3. $C_{21}H_{13}OCl$ requires Cl, 11·2%).

9 : 10-*Dichloro*-9 : 10-*dihydroanthraphenone*.—A solution of anthraphenone (11·4 g.) in carbon tetrachloride (40 c.c.) was cooled in ice, chlorine in carbon tetrachloride solution (40 c.c.) added, the mixture kept in ice for 2 hours, and light petroleum added. The resulting solid crystallised from warm benzene–light petroleum in colourless needles, m. p. 110—111° (decomp.). After being kept in a vacuum desiccator for 2 days, the substance smelled strongly of benzoyl chloride, so the sample for analysis was recrystallised from benzene and light petroleum and dried in a vacuum desiccator for 3½ hours (Found : Cl, 19·8. $C_{21}H_{14}OCl_2$ requires Cl, 20·1%).

The dichloride (0·5 g.) was suspended in cold pyridine (1 c.c.) and after an hour ether was added and the solid recrystallised from alcohol and ether. It formed colourless needles completely soluble in water, and although analysis showed that the substance was not pure it was evident that both chlorine atoms of the dichloride had suffered displacement by pyridinium groups (Found : Cl, 14·4. $C_{31}H_{24}ON_2Cl_2$ requires Cl, 13·9%).

Thermal Decomposition of Anthraphenone Dichloride.—The dichloride (0·1 g.) was heated to its melting point; hydrogen chloride and benzoyl chloride (identified by its smell) were then liberated. The resulting mixture was fractionally crystallised from alcohol into (*a*) 10-chloroanthraphenone, identified by the method of mixed melting points, and (*b*) slender, yellow needles, m. p. 96—98°, which gave solutions having a strong violet fluorescence. The identification was completed by direct comparison with an authentic sample of 9-chloroanthracene.

10-*Nitroanthraphenone*.—Anthraphenone, suspended in acetic acid, was slowly nitrated by nitric acid (1 mol.; *d* 1·42) in the cold without the production of an additive compound. The reaction was best completed by heating on the water-bath for a few minutes; the nitro-compound was then obtained pure without the elaborate purification recommended by Lippmann and Keppich (*loc. cit.*).

9 : 10-*Dinitro*-9 : 10-*dihydroanthraphenone*.—A stream of nitrogen dioxide (2·6 g.) prepared by heating a mixture of lead nitrate and sand, was led into a solution of anthraphenone (5·6 g.) in chloroform (10 c.c.), cooled in a freezing mixture; after an hour light petroleum was added. The resinous substance that separated became solid when ground under ether. Thrice recrystallised from chloroform

and light petroleum and dried in a vacuum desiccator, it was obtained in colourless needles, m. p. 175° (decomp.) (Found: N, 7·8. $C_{21}H_{14}O_5N_2$ requires N, 7·5%). Suspended over-night in cold pyridine diluted with alcohol, it lost nitrous acid and passed into 10-nitroanthraphenone (identified by the method of mixed melting points).

Fission of Anthraphenone Derivatives.—In order to compare the influence of the substituent in the 10-position the same conditions were employed in all cases. Krollpfeiffer (*loc. cit.*) has shown that if this substituent is hydroxyl, hydrolysis can be effected by boiling with hydrochloric acid in acetic acid, whereas anthraphenone itself is unaffected under these conditions.

10-Chloro-, 10-bromo-, and 10-nitro-anthraphenone were all recovered unchanged after 4 hours' boiling with hydrochloric acid in acetic acid. Chloroanthraphenone was not affected by heating for 5 hours at 170° with acetic acid saturated with hydrogen chloride.

Hydrolysis with sulphuric acid was attempted by boiling the substance (1 g.) with acetic acid (10 c.c.) containing sulphuric acid (1 c.c.) for ½ hour. Krollpfeiffer's observation that anthraphenone is completely decomposed into benzoic acid and anthracene was confirmed. Bromoanthraphenone and chloroanthraphenone gave tarry products (in the former case hydrogen bromide was liberated), whilst 9 : 10-dihydroanthraphenone, 10-nitroanthraphenone and 9 : 10-dibenzoylanthracene were recovered unchanged (in the last case after 3 hours' boiling).

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CLXVI.—*The Solubility of Beryllium Oxide in Solutions of its Salts.*

By NEVIL V. SIDGWICK and NEIL B. LEWIS.

AQUEOUS solutions of beryllium salts are known to be able to dissolve considerable quantities of the oxide, a property also possessed, but in a much smaller degree, by salts of iron, aluminium, and some other metals. A concentrated solution of the beryllium

salt of a strong acid continues to dissolve the basic carbonate with brisk effervescence even after the addition of more than one mole of base to each mole of salt present.

With the sulphate, Parsons (*J. Amer. Chem. Soc.*, 1904, **26**, 1433) found that the solubility of the oxide increased with the concentration of the salt, and in strong solution exceeded two moles to one mole of salt. No definite basic salts could be isolated: on dilution the more highly basic solutions gave flocculent precipitates; on evaporation all left glassy residues with varying ratios of Be : SO_4. The basic sulphates described by Berzelius and others were shown not to be definite compounds. Similar results were obtained with the oxalate (Parsons and Robinson, *ibid.*, 1906, **28**, 555). Parsons, Robinson, and Fuller (*J. Physical Chem.*, 1907, **11**, 651) showed that the f. p. of beryllium sulphate solution is slightly raised by the addition of the oxide, and its conductivity slightly diminished; they concluded that the basic solutions are not colloidal, since they cannot be separated by dialysis, and are not coagulated by electrolytes. The only suggestion they make to explain the results is that the salt solution acts as a mixed solvent, the oxide dissolving in the salt as camphor dissolves in acetic acid even when it is diluted with water.

Recently Britton (J., 1925, **127**, 2121) has examined electrometrically the effect of adding sodium hydroxide to beryllium sulphate solution. He finds that no precipitation occurs until 1·04 moles of sodium hydroxide have been added for each mole of beryllium sulphate. He concludes that the solution is mainly colloidal, although he admits that it is not coagulated by electrolytes and that it "betrays no sign of colloidality."

We have examined the question by measurements of (1) the solubilities and (2) the viscosities and conductivities of these basic solutions. Parsons's investigation of the system BeO,SO_3,H_2O did not extend beyond solutions containing 5% $BeSO_4$, and his results were vitiated, as he admits, by the absence of any definite solid phase. The only such phase appears to be the normal sulphate $BeSO_4,4H_2O$, and we have therefore determined the effect of addition of the oxide on the solubility of this salt: similar measurements were also made with the selenate and the oxalate. As the existence of an acid oxalate has been asserted and denied, the system $BeC_2O_4,H_2C_2O_4,H_2O$ also was examined.

In addition, the conductivities of neutral and basic chloride and oxalate solutions and the viscosities of neutral and basic chloride, oxalate, sulphate, and selenate solutions were measured.

Experimental.

Solubility of Beryllium Sulphate.—The sulphate was purified by recrystallisation from water. The hydroxide, precipitated with ammonia, was dissolved in ammonium carbonate, precipitated as the basic carbonate by passing in a current of steam, washed, and heated for several hours in water through which a current of air was drawn.

Suitable complexes were made by dissolving this basic carbonate in concentrated solutions of the sulphate, boiling to expel carbon dioxide, and filtering. They were rotated in the thermostat at 25·00° ± 0·05° in rubber-stoppered tubes for periods varying from 20 hours for the more dilute to 200 hours for the most concentrated and viscous solutions, from which the salt crystallised rather slowly. For each analysis two samples were withdrawn through cotton-wool filters into calibrated pipettes, and weighed, giving approximate values of the density. One of these was evaporated to dryness with excess of sulphuric acid and weighed as $BeSO_4$ (which is stable up to 500° : Kraus and Gerlach, *Z. anorg. Chem.*, 1924, **140**, 69) or heated in a muffle and weighed as BeO. In the other, the SO_4 was determined with barium chloride. The moist solids obtained by filtration were analysed in the same way. The increasing viscosity made it impossible to measure the complete isotherm. The solid phase was shown by the residue method to be in all cases $BeSO_4,4H_2O$. As the amount of dissolved beryllium oxide is obtained by difference, and also on account of its very low equivalent weight, the experimental error is necessarily large.

The results are in Table I.

Table I.

Solubility of $BeSO_4,4H_2O$ in presence of BeO.

	Per cent.			Molecular ratio.	
$d_4^{25°}$.	$BeSO_4$.	BeO.	Extra $BeSO_4$.	BeO : $BeSO_4$.	BeO : extra $BeSO_4$.
1·278	29·74	—	—	—	—
1·318	31·73	2·16	1·99	0·286	4·55
1·327	32·12	2·62	2·38	0·343	4·62
—	33·86	4·03	4·12	0·500	4·11
1·347	34·55	4·26	4·81	0·517	3·75
—	34·87	5·02	5·13	0·605	4·11
—	36·46	6·10	6·72	0·703	3·81
1·416	37·48	7·73	7·74	0·867	4·19
				Mean	4·14

The solubility of the pure sulphate at 25° was found to be 29·74%, which agrees fairly well with the value, 29·94%, obtained by Britton and Allmand (J., 1921, **119**, 1463).

In the last column is given the molecular ratio of the oxide present to the increase of solubility of the sulphate. It thus appears that 1 molecule of salt dissolves for every 4 molecules of oxide added.

In the analogous case of increasing solubility of lead acetate in the presence of lead oxide (Jackson, *J. Amer. Chem. Soc.*, 1914, **36**, 2346) the results calculated in this way show a much more rapid increase of solubility (about 3 moles of acetate to one of oxide).

To see whether the effect is general, other beryllium salts should be examined. Most of the salts, however, are excessively soluble, and many (*e.g.*, the chloride) crystallise with difficulty, especially in presence of the base. The perchlorate, $Be(ClO_4)_2,4H_2O$, was prepared, but its solubility at 25° was found to be 59·5% (anhydrous salt). The *benzenesulphonate* and the p-*toluenesulphonate*, which have not been previously described, were prepared by crystallisation from a solution of the basic carbonate in slightly more than its equivalent of the acid. These salts gave off their water of crystallisation at 100°; decomposition also commenced at that temperature. The salts were recrystallised from water. The *benzenesulphonate* formed small, elongated tablets [Found: BeO, 6·3. $Be(C_6H_5{\cdot}SO_3)_2,4H_2O$ requires BeO, 6·33%. Solubility at 25° = 53·8% (of anhydrous salt)]. The p-*toluenesulphonate* formed a mass of minute crystals which were only slightly denser than their saturated solution [Found: BeO, 5·9. $Be(C_7H_7{\cdot}SO_3)_2,4H_2O$ requires BeO, 5·91%. Solubility at 25° = 39·2% (of anhydrous salt)].

The great solubility of these three salts, and the difficulty of estimating the anions accurately, make them unsuitable: the only suitable salts seem to be the selenate and oxalate.

Solubility of Beryllium Selenate.—The salt was prepared by dissolving the basic carbonate in a slight excess of selenic acid, made by the oxidation of selenious acid with chloric acid (Meyer and Moldenhauer, *Z. anorg. Chem.*, 1921, **116**, 193), and was twice recrystallised from water. It was free from selenite, and had the composition $BeSeO_4,4H_2O$ (Found: BeO, 11·3; Se, 35·4; H_2O, 32·7. Calc.: BeO, 11·15; Se, 35·3; H_2O, 32·1%). The selenate was determined by reduction to selenium (Jannasch and Müller, *Ber.*, 1898, **31**, 2388). The salt loses rather more than half its water at 100—105°, and the rest at 300°, at which temperature the anhydrous salt is quite stable.

The solubilities were measured as before. The results at 25° are in Table II, each being the mean of two determinations.

The molecular ratio is the same as with the sulphate, within the limits of experimental error.

TABLE II.

Solubility of $BeSeO_4,4H_2O$ in presence of BeO.

Per cent.			Molecular ratio.	
$BeSeO_4$.	BeO.	Extra $BeSeO_4$.	BeO : $BeSeO_4$.	BeO : extra $BeSeO_4$.
36·22	0·046	—	0·008	—
37·05	0·60	0·83	0·098	4·0
38·84	1·98	2·62	0·311	4·5
40·23	2·98	4·01	0·451	4·4
42·11	3·71	5·89	0·536	3·8
				Mean 4·2

Solubility of Beryllium Oxalate.—The salt was prepared from the basic carbonate and slightly more than its equivalent of oxalic acid and the measurements were carried out in the same way as before. Parsons and Robinson (*loc. cit.*) state that the slightest excess of base entirely prevents the crystallisation of the oxalate. This was not confirmed, although the crystallisation from the more basic solutions is rather slow, lasting about a day.

The results at 25° are in Table III.

TABLE III.

Solubility of $BeC_2O_4,3H_2O$ in presence of BeO.

	Per cent.			Molecular ratio.	
$d_4^{25°}$.	BeC_2O_4.	BeO.	Extra BeC_2O_4.	BeO : BeC_2O_4.	BeO : extra BeC_2O_4.
1·179	28·20	0·08	—	0·011	—
1·224	31·73	1·31	3·53	0·160	1·35
1·259	35·01	2·35	6·81	0·260	1·29
1·282	37·17	3·23	8·97	0·337	1·36
—	41·69	4·02	13·49	0·373	(1·13)
1·290	38·20	3·52	10·00	0·367	1·33
					Mean 1·33

The analysis of the moist solids from experiments 2, 3, and 4 showed the solid phase to be in each case the normal oxalate $BeC_2O_4,3H_2O$. In calculating the results in the last column, the small quantity of oxide present in the first experiment was subtracted. The calculated solubility of the pure oxalate at 25° is 27·97%.

The oxalate thus resembles the sulphate and selenate in that its solubility is increased by the addition of the oxide, but the rate of increase is three times as great: 3 molecules of salt for every 4 molecules of oxide added.

In view of the possible formation of complex oxalates, the system was examined on the acid side ($BeC_2O_4,H_2C_2O_4,H_2O$). Rosenheim and Woge (*Z. anorg. Chem.*, 1897, **15**, 283) obtained from a solution containing excess of oxalic acid crystals of the composition

$2BeC_2O_4,H_2C_2O_4,5H_2O$. Parsons and Robinson (*loc. cit.*) could not obtain this, but only mixtures of crystals which were recognised under the microscope as those of the normal oxalate and of oxalic acid; they observed that the last traces of oxalic acid were very difficult to remove from the salt by recrystallisation. Wirth (*Z. anorg. Chem.*, 1914, **87**, 7) found the solubility of $BeC_2O_4,3H_2O$ in water at 25° to be 24·85% (of anhydrous salt), and in $N/10$-oxalic acid 27·75%, from which he concludes that complex acid salts are formed. The former value does not agree with our results, but the latter does, our values for the corresponding solubilities being 27·8% and 27·5%, respectively.

The system $BeC_2O_4,H_2C_2O_4,H_2O$ was measured at 25° by the methods already described. The complexes were heated until homogeneous, and rotated 18—36 hours in the thermostat to crystallise. The results are in Table IV. Compositions are in weights %.

TABLE IV.

System BeC_2O_4–$H_2C_2O_4$–H_2O at 25°.

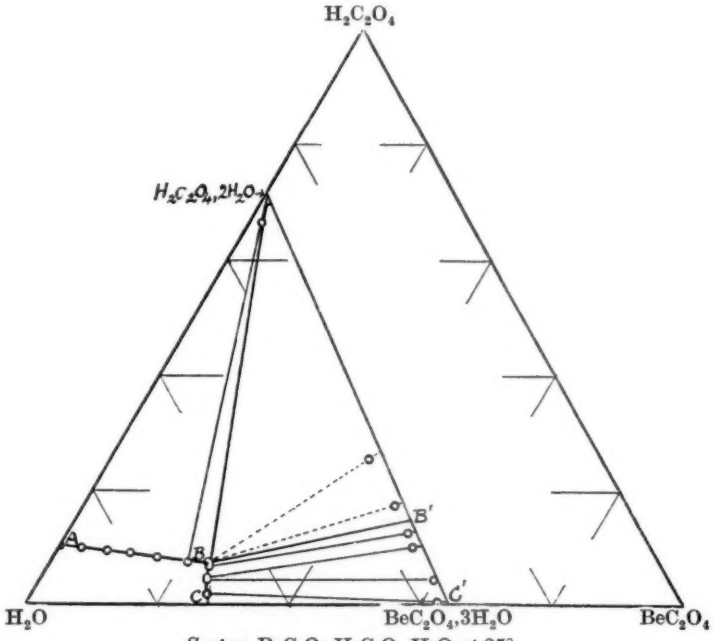
		Percentage composition.			
		Solution.		Moist solid.	
No.	$d_4^{25°}$.	BeC_2O_4.	$H_2C_2O_4$.	BeC_2O_4.	$H_2C_2O_4$.
1	1·178	26·55	1·81	62·18	0·45
2	1·187	25·33	4·42	59·85	4·40
3	1·188	25·23	4·79	53·57	10·11
4	1·197	24·49	6·88	51·53	12·68
5	1·184	23·90	7·51	47·15	17·60
6	1·197	24·01	7·46	39·11	25·38
7	1·168	20·78	7·63	1·90	66·76
8	1·139	15·79	8·46	—	—
9	1·112	11·24	9·07	—	—
10	1·087	7·60	9·52	—	—
11	1·064	3·45	10·03	—	—
12	1·043	0·00	10·23	—	—

The results are plotted in Fig. 1. The curve AB gives solutions in equilibrium with $H_2C_2O_4,2H_2O$; curve BC those in equilibrium with solids ranging from B′ to C′ which are obviously mixed crystals of $BeC_2O_4,3H_2O$ and $H_2C_2O_4,2H_2O$. It will thus be seen that there is no evidence for the existence of an acid salt such as that described by Rosenheim and Woge. This mixed crystal formation also explains the difficulty of Parsons and Robinson in removing the last of the oxalic acid impurity from beryllium oxalate by recrystallisation. It is very unusual for a salt to form mixed crystals with its own acid.

Measurement of Viscosities.—Concentrated solutions of the sulphate and the selenate were made up from the crystalline salts; those of the chloride and oxalate by dissolving the basic carbonate

in the necessary amount of acid, and determining the composition by analysis. The basic solutions, likewise analysed, were made up in the same way. They were all carefully filtered, and the dilute solutions made up from them by weight. The densities were measured in a pyknometer, and the viscosities in an Ostwald viscometer of period 84·6 seconds with water at 25°. Every value is the mean of two or more concordant results. The values given in Tables V and VI are of the equivalent normality of the salt, and of the relative viscosity (water at 25° = 1).

FIG. 1.



System $BeC_2O_4,H_2C_2O_4,H_2O$ *at* 25°.

It will be seen that the increase of viscosity caused by the base in dilute solutions is relatively small, and is little affected by the nature or concentration of the salt. The viscosity of the solution did not change on standing, or on heating to 100° and cooling again, which indicates that the phenomenon is not colloidal.

Conductivities.—These were measured in the usual way for neutral and basic chloride and oxalate solutions made up and analysed as above described, the results being given in Tables VII—X. The conductivity of the water (1·3 to 1·9 $\times$ 10^{-6}) was subtracted. The concentrations are equivalent normalities of salt present; the

TABLE V.

Viscosities of neutral and basic solutions of beryllium chloride.

Equivalent normality.	$d_{25°}^{25°}$.	Relative viscosity (water at 25° = 1).	Composition of solution.
0·338	(1·0089)	1·076	Neutral (equivalents Be : Cl = 0·997 : 1·000).
0·683	(1·0178)	1·170	
1·014	1·0265	1·245	
1·936	1·0494	1·524	
2·770	1·0700	1·816	
3·810	1·0948	2·255	
5·308	1·1295	3·065	
7·671	1·1852	5·184	
0·569	1·0182	1·153	Basic (0·476 mole BeO per mole $BeCl_2$).
1·209	1·0394	1·355	
2·255	1·0721	1·761	
3·274	1·1009	2·299	
4·757	1·1437	3·485	
5·990	1·1780	4·943	
7·539	1·2242	8·005	
0·590	(1·0223)	1·192	Basic (0·987 mole BeO per mole $BeCl_2$).
0·899	(1·0339)	1·295	
1·741	(1·065)	1·653	
2·460	1·0902	2·056	
3·602	1·1311	2·970	
4·633	1·1662	4·299	
4·955	1·1762	4·836	
6·028	1·2110	7·322	
7·350	1·2550	13·36	
0·0472	1·0022	1·016	Basic (1·760 moles BeO per mole $BeCl_2$).
0·1080	1·0050	1·036	
0·340	1·0160	1·114	
0·641	1·0301	1·238	
1·055	1·0489	1·441	
1·738	1·0792	1·893	
4·190	1·1855	6·968	

conductivities are also equivalent. The fourth column gives the product of the conductivity and the viscosity. Temperature 25° ± 0·02°. The values for the chloride solutions are in Tables VII and VIII (b = moles of BeO per mole of salt).

In Fig. 2, the product of equivalent conductivity and viscosity is plotted against the cube root of the concentration, the crosses representing the values of Fricke and Schützdeller (*Z. anorg. Chem.*, 1924, **131**, 130) for solutions obtained by double decomposition from beryllium sulphate and barium chloride. It will be seen that the conductivity is less in the basic solutions, but only by about 5%.

The hydrogen-ion concentration in beryllium chloride solutions at 25° has been measured colorimetrically by Mr. W. J. Worboys in this laboratory (results not yet published). He finds this to vary from 1·24% of the salt concentration in $N/8$-solution to 3·68% in $N/512$. If we assume that the hydrolysis takes place thus: $BeCl_2 + H_2O = (BeOH)Cl + HCl$, the practical result will be to

Table VI.

Viscosities of neutral and basic solutions of beryllium salts.

Equivalent normality.	d_{25}^{25}.	Relative viscosity (water at 25° = 1).	Solution.
0·425	(1·019)	1·147	Beryllium sulphate (neutral).
0·644	1·0290	1·221	
1·109	1·0503	1·420	
1·737	1·0782	1·730	
2·638	1·1163	2·312	
3·874	1·1663	3·644	
5·878	1·2454	7·199	
0·455	1·0254	1·189	Beryllium sulphate basic (0·965 mole
0·666	1·0367	1·292	BeO per mole $BeSO_4$).
1·078	1·0593	1·516	
1·654	1·0900	1·926	
2·382	1·1274	2·644	
3·319	1·1747	4·069	
4·022	1·2104	5·843	
5·045	1·2601	10·20	
6·432	1·3240	22·80	
7·702	1·3783	51·1	
8·933	(1·426)	140·6	
0·457	1·0297	1·167	Beryllium selenate (neutral).
0·981	1·0634	1·386	
2·027	1·1288	1·985	
3·111	1·1950	2·903	
4·771	1·2940	5·864	
0·483	1·0373	1·215	Beryllium selenate basic (0·979 mole
0·983	1·0761	1·508	BeO per mole $BeSeO_4$).
2·130	1·1624	2·569	
3·336	1·2464	4·599	
4·737	1·3429	11·00	
0·565	1·0160	1·098	Beryllium oxalate neutral (equi-
1·138	1·0325	1·207	valents Be : C_2O_4 = 0·996 : 1·000).
2·324	1·0663	1·493	
3·671	1·1047	1·950	
4·971	1·1419	2·564	
0·556	1·0230	1·156	Beryllium oxalate (0·974 mole BeO
1·085	1·0439	1·329	per mole BeC_2O_4).
2·267	1·0896	1·909	
3·569	1·1426	3·058	
5·011	1·1980	5·757	

Table VII.

Conductivities of beryllium chloride (neutral) solutions.

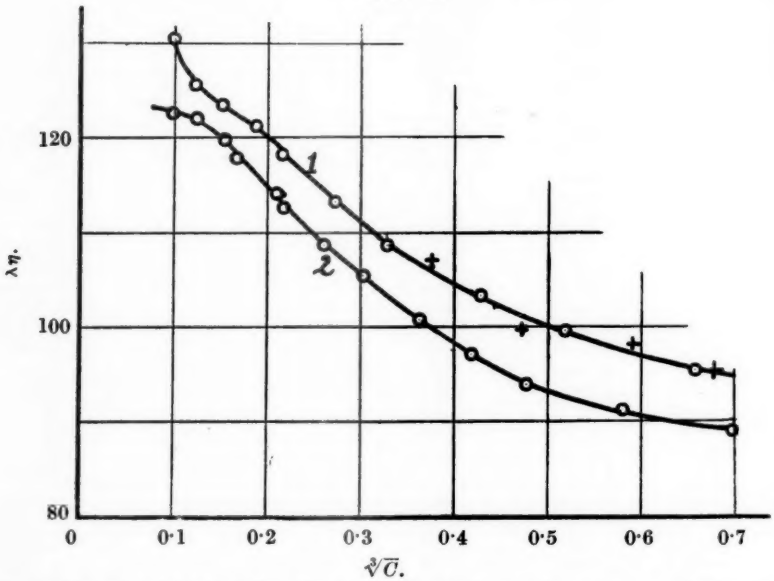
Normality.	Relative viscosity (η).	Equivalent conductivity (Λ).	$\Lambda\eta$.	$\Lambda\eta$ (corr.).
0·001001	—	130·6	130·6	115·8
0·001832	—	125·8	125·8	114·1
0·003467	(1·001)	123·4	123·5	113·7
0·006491	(1·002)	121·1	121·3	113·3
0·009964	(1·002)	118·2	118·4	111·3
0·02014	(1·005)	112·8	113·3	107·5
0·03392	(1·008)	108·1	108·9	103·9
0·07863	(1·019)	101·3	103·3	98·8
0·1387	(1·034)	96·5	99·8	95·7
0·2840	(1·069)	89·4	95·6	—
0·5548	(1·136)	81·1	92·1	—
1·0140	1·245	72·1	89·8	—

TABLE VIII.

Conductivities of beryllium chloride (basic, b = 1·760) solutions.

Normality.	η.	λ.	$\lambda\eta$.	Normality.	η.	λ.	$\lambda\eta$.
0·000967	—	122·9	122·9	0·04724	1·016	99·3	100·9
0·000972	—	122·8	122·8	0·07257	(1·025)	94·9	97·2
0·001850	—	122·2	122·2	0·1164	(1·039)	90·5	94·0
0·003568	(1·001)	119·9	120·0	0·1968	(1·066)	85·6	91·3
0·004637	(1·002)	117·8	118·0	0·3400	1·114	80·0	89·1
0·009196	(1·003)	113·7	114·0	0·6415	1·238	71·4	88·4
0·01015	(1·003)	112·3	112·6	1·0546	1·441	63·1	91·0
0·01763	(1·006)	107·9	108·6	1·738	1·893	52·7	99·9
0·02725	(1·009)	104·4	105·3	4·190	6·968	26·93	187·7

FIG. 2.



Equivalent conductivities of beryllium chloride solutions. Curve 1, *neutral solution. Curve* 2, *basic* (*b* = 1·760) *solution.*

\+ *denotes observations by Fricke & Schützdeller* (*loc. cit.*).

increase the conductivity by an amount corresponding to the hydrogen ion present. By subtracting this amount we find the conductivity of the non-hydrolysed solutions (last column in Table VII). As will be seen, this correction brings the values of the neutral very near to those of the basic solutions, except at high dilutions, where even the latter may still be perceptibly hydrolysed.

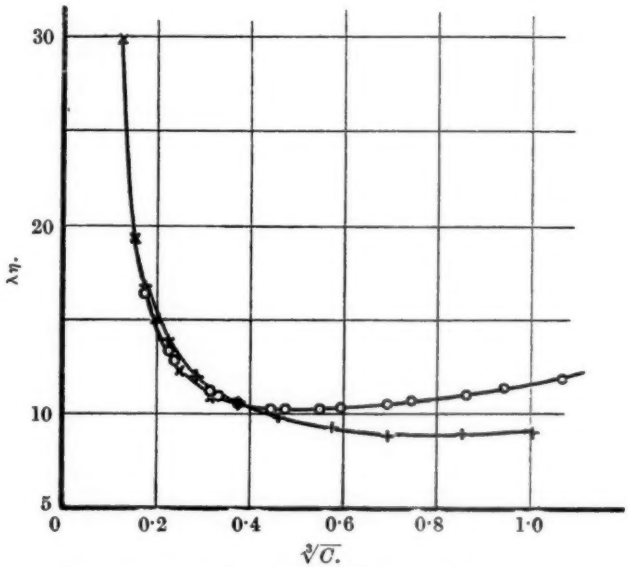
The corrected conductivities of the solutions of the neutral chloride extrapolate to a value for the mobility at 25° of $\frac{1}{2}BeCl_2$ = 118·5, corresponding to 43 for $\frac{1}{2}$Be. Fricke and Schützdeller (*loc.*

cit.) give a value of 30 for the mobility of $\frac{1}{2}Be$. This is based on their values for the conductivities of solutions from $0{\cdot}05N$ to $0{\cdot}5N$; but their correction for hydrolysis is rather uncertain, being founded on a measurement by Wood (J., 1910, **97**, 878) of its value (2·2%) at $0{\cdot}35N$, from which they calculated the values at greater dilutions.

The values for the oxalate solutions are in Tables IX and X.

The results are plotted in Fig. 3, the crosses representing those of Rosenheim and Woge (*loc. cit.*).

FIG. 3.



Equivalent conductivities of beryllium oxalate solutions.

⊙ *Neutral solutions.* × *Neutral solutions (Rosenheim and Woge).* + *Basic ($b = 0{\cdot}974$) solutions.*

TABLE IX.

Conductivities of beryllium oxalate (neutral) solutions.

Normality.	η.	λ.	$\lambda\eta$.	Normality.	η.	λ.	$\lambda\eta$.
0·00550	1·001	16·38	16·39	0·1657	1·028	9·95	10·22
0·01407	1·002	12·81	12·83	0·2136	1·036	9·97	10·32
0·01180	1·002	13·32	13·35	0·3351	1·057	9·95	10·51
0·03202	1·005	11·08	11·13	0·4164	1·072	9·99	10·71
0·03732	1·006	10·87	10·93	0·6478	1·115	9·87	11·00
0·05323	1·009	10·49	10·58	0·8372	1·149	9·94	11·42
0·08931	1·015	10·12	10·27	1·1403	1·209	9·67	11·69
0·1084	1·019	10·09	10·28				

TABLE X.

Conductivities of beryllium oxalate (basic, b = 0·974) solutions.

Normality.	η.	λ.	$\lambda\eta$.	Normality.	η.	λ.	$\lambda\eta$.
0·00574	1·001	16·79	16·81	0·1897	1·052	8·85	9·31
0·01144	1·003	13·93	13·98	0·3397	1·094	8·02	8·78
0·02359	1·007	11·88	11·96	0·6236	1·178	7·60	8·95
0·05392	1·015	10·35	10·51	1·0245	1·307	6·90	9·02
0·1012	1·028	9·53	9·80				

The conductivities of the oxalate are very small, as may be seen by comparing them with those of the sulphate (Ley, *Z. physikal. Chem.*, 1899, **30**, 245) at the same dilutions.

Dilution (litres per equiv.)	32	128	512
Equiv. cond. of sulphate	66·4	88·7	112·6
„ „ of oxalate	10·8	15·1	29·8

Further, the equivalent conductivity of the oxalate solution increases at concentrations above about 0·15*N*, which behaviour is probably unprecedented.

Freezing Points of Oxalate Solutions.—The depression of freezing point of aqueous solutions of the oxalate was measured in a Beckmann apparatus. The results are

Mole of salt per 1000 g. of water.	Δ.	Molecular depression.	i.
0·0224	0·048°	2·14°	1·15
0·0532	0·119	2·24	1·20
0·1049	0·220	2·10	1·13
0·1771	0·363	2·05	1·10
0·3665	0·720	1·96	1·05

The values of the van 't Hoff factor i are, in the stronger solutions, of the same order as those observed by Parsons, Robinson, and Fuller (*loc. cit.*), but at greater dilutions they are considerably lower.

Discussion of Results.

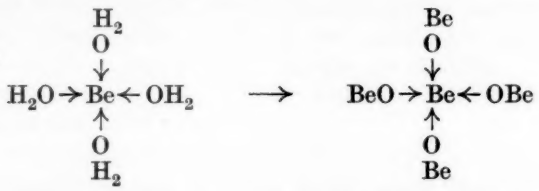
(1) *Sulphate, Selenate, and Chloride.*—The solubility of beryllium oxide in solutions of its salts may be due to three causes. (1) The salt may make the oxide form a colloidal solution; (2) the oxide may form a basic salt, for example of the univalent ion $[BeOH]^+$, or (3) it may attach itself to one of the ions of the normal salt, in which case, since the property is common to beryllium salts in general, it must combine with the beryllium ion. The first hypothesis, that of colloid formation, has not been entirely disproved. The most basic solutions are somewhat turbid, and although they cannot be separated by dialysis, they may contain some colloidal material. But the whole of the dissolved oxide cannot be in this form. Some of the solutions described above contain more than 2, and they can be prepared with as many as 5 moles of oxide per

litre, a concentration enormously greater than is reached by the colloidal solutions of other metallic hydroxides. Further, the stability of these solutions to the action of heat and of electrolytes is against the view that they are highly concentrated colloids, a view which also fails to explain why the salt is more soluble in presence of the oxide. The bulk of the oxide must be present in some other form. (2) The formation of basic salts of an ion $[BeOH]^+$ would not allow of the solution of more than one mole of oxide for every mole of salt, whereas more basic solutions can be prepared. It would also involve an increase of one ion for every molecule of oxide dissolved—$[Be]A + Be(OH)_2 = [BeOH]_2A$—and hence the addition of oxide should lower the freezing point and probably increase the conductivity, whereas it actually has the opposite effect.

We are therefore left with the third hypothesis, that the oxide combines with the beryllium ion to form a complex kation $[Be,xBeO]^{++}$. This would account for the small change in conductivity (3—7%, mainly due to the disappearance of hydrolysis), since the number of ions would not alter, but the " beryllated " ion might have a slightly different mobility and degree of ionisation. It is also supported by the slight decrease (about 10%) in the freezing point depression of the sulphate observed by Parsons, Robinson, and Fuller (*loc. cit.*). It explains the increase in the solubility of the salt in presence of the oxide as due to the formation of a new complex salt. If we could assume the solubility of the normal salt to be the same in presence of the complex salt as in water, the molecular ratio of the added oxide to the increased solubility of the salt (4·14 with the sulphate and 4·2 with the selenate) would indicate that the complex ion was $[Be,4BeO]^{++}$. The accompanying increase of the anion in the basic solution must, however, somewhat diminish the solubility of the normal salt, although we cannot at such high concentrations calculate the magnitude of this effect. Hence the observed ratio of 4·14 or 4·2 must be greater than the average number of BeO molecules attached to a " beryllated " Be ion.

Now there is good evidence that while the covalency of beryllium cannot exceed 4, it has a strong tendency, particularly in the ionised state, to reach this value. Its soluble salts never have more than 4 molecules of water, but seldom fail to attain this number (the case of the oxalate is discussed below). The same tendency of the atom to pass from the ionised to the covalent state is shown by the low conductivity of the fused chloride and the stability of many of its covalent organic compounds (*e.g.*, the non-ionised basic acetate). Its oxide may thus be expected readily

to assume the covalent form Be=O, which could replace the water of crystallisation of the ion:



This replacement will no doubt be incomplete, a series of mixed ions being formed, with the water only partly replaced by BeO, so that on the average there will be less than 4 BeO groups attached to each " beryllated " ion, as we find to be the case.

(2) *Beryllium Oxalate.*—The above hypothesis accounts for the behaviour of basic solutions of the sulphate, selenate, and chloride, and should be applicable to any solution containing beryllium ion: but the behaviour of the oxalate, which increases in solubility by about 3 molecules for every 4 of the oxide added, needs further explanation. This salt is peculiar in many ways. It is unique among the oxalates of bivalent metals in being very soluble in water (nearly 30% at 25°): the oxalates of Mg, Ca, Sr, Ba, Zn, Cd, Hg″, Sn″, Cr″, Mn″, Fe″, Co″, and Ni are all very slightly if at all soluble. It is also almost unique among beryllium salts in not forming a tetrahydrate but only a trihydrate. These facts clearly indicate that it is not a normal oxalate. Further peculiarities which we have found are (1) the conductivity, which even at $V = 512$ is barely a quarter of that of the sulphate, and at greater concentrations falls to about a sixth, showing that (assuming the ionic mobilities to be about the same) the number of ions formed is only about a quarter of that produced by a normal bi-bivalent salt. (2) The increase of solubility of the salt on addition of oxide is three times as great as with the sulphate or selenate (1 : 1·3 instead of 1 : 4·1). (3) Finally the f. p. experiments show that the number of molecules (including ions) in the solution is not much less than it would be with a normal salt.

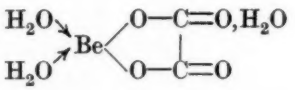
The last fact proves that the compound formed cannot have a high molecular weight, and suggests that the ions have combined to form a non-polar molecule:

$$Be[C_2O_4] \longrightarrow [BeC_2O_4]$$

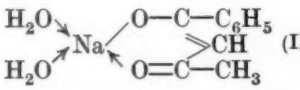
which is not improbable in view of the strong tendency (already mentioned) of the beryllium ion to pass into the covalent state, and that of the oxalate ion to form a covalent oxalato-ring, as in Werner's optically active $K_3[Cr(C_2O_4)_3]$. On this simple assumption

we should conclude, since the conductivity is reduced to about a quarter, that the solution contains about 3 molecules of oxalato-compound to 1 molecule of salt. The value of i found by the f. p. method would be $1 + \frac{1}{4}\alpha$, if α is the true degree of dissociation of the salt: the observed values of i are from 1·2 at 0·05 molar normal to 1·1 at 0·37. This assumption is further supported by the fact that the compound crystallises with 3 molecules of water. The oxalate group is usually monohydrated, both as an ion and in oxalato-compounds: for example, we have $K_2C_2O_4,H_2O$; $(NH_4)_2C_2O_4,H_2O$; $(NH_4)_2[Hg(C_2O_4)_2],2H_2O$; K_3 and $(NH_4)_3[Cr(C_2O_4)_3],3H_2O$, all salts of kations which are rarely if ever hydrated. Thus one of the H_2O molecules can be attached to the oxalate group. The other two must be joined to the beryllium atom (formula I) if it is to have the stable covalency of 4 which beryllium always attains if possible, and the attainment of which always promotes the formation of covalent links, as in the sodium compound of benzoylacetone (Sidgwick and Brewer, J., 1925, **127**, 2383); this when anhydrous is a salt, but it readily takes up two molecules of water and becomes covalent (formula II), as is shown by its then being soluble in hydrocarbons.

(I.)



(II.)



A non-polar structure of this kind also makes the formation of solid solutions with oxalic acid less inexplicable.

One peculiarity of the oxalate is unexplained: the large increase (1 : 1·3 instead of 1 : 4·1) of solubility on addition of the oxide. If the latter combines only with the beryllium ion, as it does in the solutions of the strong acid salts, the ratio should be the same in both cases; for on the removal of part of the ions in the "beryllated" form, the equilibrium between the polar and non-polar modifications will be restored. The only explanation would seem to be that the oxide mainly combines with the non-polar form in the ratio 1 : 1 (presumably replacing a molecule of water), but partly also with the ion, as in the sulphate and selenate, thus lowering the ratio of increased solubility to added oxide from 1 : 1 to 1 : 1·3.

The peculiar form of the conductivity curve, which scarcely falls (and if corrected for viscosity, rises) from $N/5$- to N-solution, seems to be without parallel. Since with increasing concentration the molecular conductivity of the true salt must diminish (as it does with all other salts), and likewise presumably the proportion of true salt to non-polar compound, some other reaction must intervene; but it is difficult to see what this is.

Our thanks are due to Messrs. Brunner Mond and Co. for a grant towards the cost of this work, and one of us (N. B. L.) wishes to express his gratitude to the Commissioners of the 1851 Exhibition for a scholarship which made it possible for him to take part in it.

DYSON PERRINS LABORATORY,
OXFORD. [*Received, March 19th*, 1926.]

CLXVII.—*ω-Mono- and Dibromo-derivatives of Quinaldine and Nitroquinaldines and their Products of Hydrolysis.*

By DALZIEL LLEWELLYN HAMMICK.

IT has been shown (J., 1923, **123**, 2882) that quinaldine can readily be brominated to ω-tribromoquinaldine, which can be hydrolysed to quinaldinic acid. A similar route to the corresponding α-aldehyde and alcohol has now been investigated. Unfortunately, quinaldine cannot be selectively brominated to the *ω-mono-* and *dibromo-*derivatives; ω-tribromo-quinaldine, however, can be reduced to the two other ω-bromoquinaldines by the action of the calculated quantities of titanous or stannous chloride in alcoholic or acetone solution. ω-Dibromoquinaldine can also be obtained in about 60% yield by the action of excess of sodium arsenite on the tribromo-compound in aqueous-alcoholic solution.

Unlike ω-tribromoquinaldine, the mono- and dibromo-derivatives cannot be hydrolysed by the action of acids; even oleum acting at 50° for 12 hours is ineffective. Alkalis yield coloured and resinous products. Silver nitrate, however, in aqueous alcohol converts these derivatives quantitatively into the alcohol and aldehyde respectively.

The mononitro-compounds obtained by the direct nitration of quinaldine have been directly brominated to the ω-di- and tribromo-derivatives. The latter, on hydrolysis, yield nitrocarboxylic acids which give nitroquinolines on fusion; these have been identified as the 5- and 8-nitro-compounds. The orientation of the products of the direct nitration of quinaldine given by Decker and Remfrey (*Ber.*, 1905, **38**, 2773) is thus confirmed.

EXPERIMENTAL.

ω-Dibromoquinaldine.—A solution of 23·7 g. (2 mols.) of stannous chloride in 100 c.c. of acetone was slowly added, with constant shaking and cooling, to 20 g. (1 mol.) of ω-tribromoquinaldine

(*loc. cit.*) in 250 c.c. of acetone. After 1 hour, the acetone was removed, the solution neutralised with chalk and distilled with steam for about 9 hours. The white, crystalline solid in the distillate crystallised from ligroin in colourless needles, m. p. 120° (yield 9·0 g.; 60%) (Found: Br, 52·8. $C_{10}H_7NBr_2$ requires Br, 53·1%).

Quinoline-2-aldehyde.—A mixture of ω-dibromoquinaldine (8 g.) in 50 c.c. of boiling alcohol with 8·6 g. (2 mols.) of silver nitrate in 10 c.c. of hot water was boiled for 10 minutes and, after addition of hydrochloric acid and filtration, distilled with steam to remove the alcohol. The solution was now neutralised with chalk and again distilled with steam; the oil that slowly solidified in the distillate separated from ligroin in colourless crystals, m. p. 71° (yield 4·6 g.; 100%) (Found: N, 8·9. Calc. for $C_9H_6N{\cdot}CHO$: N, 8·0%). The aldehyde gave an oxime, m. p. 184°, and a phenylhydrazone, m. p. 204° (compare Kaufmann and Vallette, *Ber.*, 1913, **46**, 56).

ω-*Monobromoquinaldine* was prepared exactly as ω-dibromoquinaldine, twice the amount of stannous chloride in acetone solution being used. The *monobromoquinaldine* distilled in steam as a readily solidifying oil and crystallised from ligroin in colourless needles, m. p. 83° (Found: Br, 36·1. $C_{10}H_8NBr$ requires Br, 36·0%). The yield was about 50%.

ω-*Hydroxyquinaldine* was obtained in quantitative yield from ω-monobromoquinaldine by the action of the calculated quantity of silver nitrate in alcoholic solution, exactly as in the preparation of quinoline-2-aldehyde (*vide supra*). The *carbinol* is volatile in steam and crystallises from ligroin or alcohol in fine needles, m. p. 64° (Found: N, 8·65. $C_9H_6N{\cdot}CH_2{\cdot}OH$ requires N, 8·8%). It is readily oxidised by chromic acid to quinoline-2-aldehyde.

ω-*Tribromo-8-nitroquinaldine.*—A solution of quinaldine in excess of cold concentrated sulphuric acid was shaken with the calculated quantity of potassium nitrate crystals until these had dissolved. After heating for 20 minutes on the water-bath, the mixture was poured into water and nearly neutralised with sodium hydroxide, whereupon 8-nitroquinaldine separated (compare Doebner and Miller, *Ber.*, 1884, **17**, 1700, who added quinaldine nitrate to concentrated sulphuric acid). A solution of 7 g. of the recrystallised nitroquinaldine (m. p. 130°) in 150 c.c. of glacial acetic acid saturated with sodium acetate was slowly treated with 20 g. (3 mols.) of bromine in 50 c.c. of glacial acetic acid. After 20 minutes' heating on the water-bath, the mixture was poured into water; the ω-*tribromo-8-nitroquinaldine* that separated crystallised from alcohol in faintly yellow needles, m. p. 132° (yield 100%) (Found: N, 6·5. $C_{10}H_5O_2N_2Br_3$ requires N, 6·6%).

8-*Nitroquinaldinic Acid.*—ω-Tribromo-8-nitroquinaldine (10 g.)

was boiled with 20% sulphuric acid for 10 hours; the 8-nitroquinaldinic acid obtained on pouring the mixture into water and partly neutralising it separated from alcohol in almost colourless crystals, m. p. 182° (Besthorn and Ibele, *Ber.*, 1906, **39**, 2329, give m. p. 177°). The acid on fusion gave 8-nitroquinoline which, recrystallised from ligroin, melted at 89° alone or mixed with a pure specimen.

ω-*Dibromo*-8-*nitroquinaldine* was prepared in the same way as ω-tribromo-8-nitroquinaldine, except that two molecular proportions of bromine were used instead of three. The compound crystallises from alcohol in pale yellow needles, m. p. 183° (Found: N, 7·9. $C_{10}H_5O_2N_2Br_2$ requires N, 8·1%).

8-*Nitroquinoline*-2-*aldehyde*.—Hydrolysis of ω-dibromo-8-nitroquinaldine in the usual way with alcoholic silver nitrate gave about 50% yields of 8-*nitroquinoline*-2-*aldehyde*, which crystallises from alcohol in golden needles, m. p. 152° (Found: N, 13·7. $C_9H_5O_2N_2$·CHO requires N, 13·9%).

ω-*Tribromo*-5-*nitroquinaldine*.—The second nitroquinaldine, m. p. 82°, obtained by the direct nitration of quinaldine is described by Doebner and Miller (*loc. cit.*) as the 7-nitro-compound. The bromination of this substance does not proceed so readily or so smoothly as in the cases already described and the products were obtained in poor yield and mixed with much gummy material. A solution of 11 g. of the above nitroquinaldine in glacial acetic acid saturated with sodium acetate was slowly treated with 28 g. (3 mols.) of bromine in 75 c.c. of acetic acid. After heating for an hour on the water-bath, the mixture was poured into water. The gummy mass that separated was extracted with hot alcohol, from which an oil separated on cooling. The oil solidified on keeping and after recrystallisation from ligroin melted at 93° (yield 4 g.; 17%) (Found: N, 6·5. $C_{10}H_5O_2N_2Br_3$ requires N, 6·6%).

This ω-tribromonitroquinaldine was boiled for 10 hours with 20% sulphuric acid. The solution on neutralisation gave an acid which was not purified but, after drying, was decarboxylated by fusion; the product, crystallised from ligroin, melted at 72° alone or mixed with pure 5-nitroquinoline. Doebner and Miller's "7-nitroquinaldine" is thus shown to be the 5-nitro-derivative, in accordance with the conclusions of Decker and Remfrey (*loc. cit.*).

Acknowledgment is made of a grant from the Chemical Society which has partly defrayed the cost of this investigation.

THE DYSON PERRINS LABORATORY,
OXFORD.

[*Received, March 24th*, 1926.]

CLXVIII.—*The Nature of the Alternating Effect in Carbon Chains. Part IV. Some Abnormal Reactions as Evidence of the Incipient Ionisation of Certain Hydrogen Atoms in Hydrocarbon Radicals.*

By Eric Leighton Holmes and Christopher Kelk Ingold.

Hydrolytic reactions have often been utilised to diagnose the relative polarities of atoms in combination, the residue which, after fission, appears in association with hydrogen being regarded as negative in comparison with the other:

$$\overset{+}{A} - \overset{-}{B} + H_2O \longrightarrow \overset{+}{A}\cdot OH + H\cdot\overset{-}{B}.$$

Observations are recorded in this paper which show that, in certain circumstances, the direction of fission may be changed by altering the experimental conditions even in cases in which the relative polarity of the atoms at the point of fission is fixed by the presence, according to modern theory, of a real electrical charge on one of them.

In the following formulæ for the sulphonamide group,

the sulphur atom is represented as carrying a double positive charge, and each of the oxygen atoms a single negative one, whilst the nitrogen atom remains neutral. That is to say, the sulphur atom is necessarily positive with respect to the nitrogen atom, and, accordingly, a sulphonic acid and an amine, $R\cdot SO_2-OH + H-NR'R''$, are the expected products of fission.

p-Toluenesulphonbenzylmethylamide (I) behaves in this way on treatment with mineral acids, but with concentrated alkalis it gives products equivalent, as regards state of oxidation, to a sulphinic acid and a hydroxylamine, $RSO_2-H + HO-NR'R''$. Two of the products obtained, toluene and sulphurous acid, must almost certainly have been formed from *p*-toluenesulphinic acid, which is known to undergo decomposition into these substances in the presence of strong alkalis; whilst the third, benzylidenemethylamine, is the expected dehydration product of benzylmethylhydroxylamine. The possibility of its formation from the hydroxylamine under the conditions used was controlled by subjecting the

dibenzylhydroxylamine to the same conditions, when benzylidenebenzylamine was obtained.

$$C_6H_4Me\cdot SO_2\cdot N\begin{cases}CH_3 \xrightarrow{HCl} C_6H_4Me\cdot SO_3H + NH(CH_3)\cdot CH_2Ph & \text{Type (A)}\\ CH_2Ph \xrightarrow{KOH} \{C_6H_5Me + K_2SO_3\} + N(CH_3){:}CHPh & \text{Type (B)}\end{cases}$$
(I.)

$$[C_6H_4Me\cdot SO_2H]\ [N(OH)(CH_3)\cdot CH_2Ph]$$

Precisely analogous decompositions were observed in the case of *p*-toluenesulphonbenzylamide (II), only in this instance the benzylideneimine was largely hydrolysed to ammonia and benzaldehyde, which underwent further change into benzoic acid (and, probably, benzyl alcohol) under the action of the alkali.

$$C_6H_4Me\cdot SO_2\cdot N\begin{cases}H \xrightarrow{HCl} C_6H_4Me\cdot SO_3H + NH_2\cdot CH_2Ph & \text{Type (A)}\\ CH_2Ph \xrightarrow{KOH} C_6H_5Me + K_2SO_3 + NH{:}CHPh & \text{Type (B)}\end{cases}$$
(II.)

In attempting to account for these remarkable reactions (Type B), we have formed the view that the decomposition with alkali, essentially an attack by negative hydroxyl ions, commences not at the sulphur atom (in spite of its positive polarity), but at a carbon–hydrogen linking in an alkyl group attached to the nitrogen atom.

Owing to the diminished additive power of the ionised double linkings in the sulphonic acid group (they are single linkings from the standpoint of co-valency), we regard the sulphur atom as largely protected from the direct attack of hydroxyl ions by the additive mechanism discussed by Gane and Ingold (this vol., p. 10) in connexion with the alkaline hydrolysis of carboxylic esters. The attack therefore commences, in the above instances, at the CH_2 group in which, we believe, the hydrogen atoms are in a condition of incipient ionisation, ready to give up their nuclei (but not their electrons) to a hydroxyl ion to form undissociated water (compare Goss and Ingold, J., 1925, **127**, 2777). As the extraction of a hydrogen ion from the benzyl group proceeds, a charged unsaturated residue is left, which in rearrangement necessarily gives a Schiff's base and splits off the ion of a sulphinic acid:

$$PhCH(H)\cdot NMe\cdot SO_2\cdot C_7H_7 + OH' \longrightarrow PhC(H)\cdot NMe\cdot SO_2\cdot C_7H_7' \longrightarrow PhCH{:}NMe + SO_2\cdot C_7H_7'$$

The changes here represented as taking place in steps are regarded as being actually continuous and simultaneous. According to this view, the hydroxylamine does not intervene in the formation of the Schiff's base, but the ready dehydration of hydroxylamines to

Schiff's bases under the action of alkali can be explained by a somewhat similar mechanism.

In order to test the view that the attack by hydroxyl ions commences at the benzyl group, the sulphonamides $C_6H_4Me{\cdot}SO_2{\cdot}NMePh$ (III) and $C_6H_4Me{\cdot}SO_2{\cdot}NHPh$ (IV) were treated with potash under the same conditions.

In case (III), an opportunity still remains for the suggested mechanism to function if the attack could begin at one of the hydrogen atoms of the methyl group: the initial products would be toluenesulphinic acid and methyleneaniline, and the formation of these would be shown by the identification of toluene, sulphite, formaldehyde, and aniline. However, for reasons indicated below, the extraction of a hydrogen nucleus (ion) from the methyl group would be expected to offer much greater difficulty than its extraction from the benzyl group in examples (I) and (II). Consequently fission of Type (B) should occur only to a small extent or not at all. Actually a reaction of Type (B) can be detected, but the principal change is that which corresponds with Type (A).*

In case (IV), the mechanism by which reaction (B) has been explained cannot operate at all, and actually there is no evidence of fission to form a sulphinic acid, the observed decomposition being wholly of type (A). The occurrence of reaction (A) in the last two cases and, under the influence of acids (hydrogen ions), in all four cases, we attribute to the direct ionic fission of the sulphur–nitrogen bond, a process which occurs only when more facile modes of decomposition are impossible.

In our opinion, then, the remarkable action of alkalis on the sulphonamides (I) and (II) provides clear evidence of the occurrence of the benzyl hydrogen atoms in a state of incipient ionisation. The cause of this condition we attribute to general polarity (Lewis), the inherent tendency of hydrogen to function as a positive ion (separate as a proton) being augmented by the presence of a group such as phenyl, which is assumed to be capable of drawing electrons towards itself, thus leaving the hydrogen nuclei in a loosely-combined, active state. This condition obtains in all ψ-acids, and bears on the questions of hydrogen-tautomerism and meta-substitution (next paper). The opposite condition, in which a group, by allowing electrons to be withdrawn from it, increases a pre-existing, inherent tendency for an atom or group (*e.g.*, hydroxyl) to separate as a negative ion, is similarly illustrated in ψ-bases, mobile hydroxyl tautomerism, and ortho-para-substitution (see next paper). In the first case, the activating group may be said to act as an " electron-

* Excepting that, of course, *p*-cresol and potassium sulphite are obtained in place of *p*-toluenesulphonic acid.

sink," and in the second as an "electron-source," towards the rest of the molecule:

$$\overset{+}{H}\longrightarrow C\longrightarrow X \qquad\qquad H\overset{-}{O}\longleftarrow C\longleftarrow Y$$
(ψ-*acid*) (ψ-*base*)

Experimental.

(I) *Hydrolysis of* p-*Toluenesulphonbenzylmethylamide* (I).—The amide (8 g.) was cautiously warmed with moist fused potassium hydroxide (20 g.) during about 0·5 hour, the volatile decomposition products being distilled towards the end of that period. The distillate, on being dried and redistilled, gave two fractions, b. p. 110—120° (*a*) and b. p. 180—190° (*b*). Fraction (*a*) (2·5 g.) had the odour of toluene, on redistillation boiled close to 110° and on nitration yielded 2 : 4-dinitrotoluene (m. p. 71°), which was identified by comparison with an authentic specimen. Fraction (*b*) (3·75 g.) consisted essentially of benzylidenemethylamine (Found: C, 80·4; H, 7·6. Calc.: C, 80·7; H, 7·0%). On treatment with dilute hydrochloric or nitric acid, an oil separated, which was identified as benzaldehyde by its odour, and semicarbazone (m. p. 224°, which is the correct m. p., not 214° as stated in the literature). The hydrochloric acid solution on evaporation gave methylamine hydrochloride (m. p. 226°; mixed m. p. with genuine specimen 226°. Found: Cl, 52·0. Calc.: Cl, 52·6%), and similarly, the nitric acid solution yielded methylamine nitrate (m. p. 99—101°; mixed m. p. with genuine specimen 99—101°. Found: C, 13·0; H, 7·0. Calc.: C, 12·8; H, 6·7%). An authentic specimen of benzylidenemethylamine prepared as described by Zaunschirm (*Annalen*, 1888, **245**, 281) behaved in the same way. The residual alkali on dilution and acidification evolved sulphur dioxide.

(II) *Hydrolysis of* p-*Toluenesulphonbenzylamide* (II).—The hydrolysis of 8 g. of this amide was carried out as in the previous case, but a considerable amount of ammonia was evolved. The volatile liquid products were shaken with dilute acid, and the undissolved portion was distilled; 0·9 g. of pure toluene was then obtained. The acid extract deposited benzaldehyde and gave ammonia on being made alkaline, so that the presence of benzalimine in the original distillate may be inferred. The residual alkali was extracted with ether to remove any neutral or basic products (which, however, were absent) and then acidified. The solution was boiled to expel most of the sulphur dioxide and then extracted with ether. The solid residue (1·5 g.) from the ether consisted largely of benzoic acid contaminated by some substance or substances

which instantaneously decolorised permanganate and could only be removed by distillation (b. p. 240—245°/750 mm.) followed by several crystallisations from carbon disulphide and ligroin. (Found: C, 68·6; H, 5·0; *M*, 120. Calc.: C, 68·9; H, 4·9%; *M*, 122). *p*-Cresol was searched for, but could not be detected.

(III) *Hydrolysis of* p-*Toluenesulphonphenylmethylamide* (III).—This *amide*, m. p. 93°, was prepared by the action of *p*-toluenesulphonyl chloride on a sample of Kahlbaum's methylaniline which qualitative tests showed to contain no trace of a primary base. The hydrolysis of 8 g. was carried out as before, the gas evolved being passed through Schiff's reagent acidified with dilute sulphuric acid, when a permanent red colour was produced. The volatile liquid products were separated into neutral and basic portions. The former was small in amount, had the odour of toluene, and yielded a solid which was identified as unchanged amide. The basic portion (2·9 g.) had b. p. 185—190°, and gave the qualitative reactions both of a primary and of a secondary base, and both aniline and methylaniline were identified as their *p*-toluenesulphonyl derivatives (Hinsberg's method of separation). The alkaline residue on acidification evolved sulphur dioxide, and extraction with ether yielded a dark oil which slowly deposited a small quantity of crystals, m. p. 190—200° (0·1 g.). After crystallising twice from water, these yielded prisms, m. p. 210°, which were identified as *p*-hydroxybenzoic acid by analysis (Found: C, 60·5; H, 5·0. Calc.: C, 60·8; H, 4·4%) and comparison with a genuine specimen. The oil from which the crystals separated was distilled (b. p. 190—195°) and was identified as *p*-cresol by conversion into its benzoyl derivative. *p*-Hydroxybenzoic acid is known (Barth, *Annalen*, 1870, **154**, 359) to be formed by the action of potassium hydroxide on *p*-cresol.

(IV) *Hydrolysis of* p-*Toluenesulphonanilide* (IV).—This amide (8 g., m. p. 99°) was treated as in the previous cases and the products were separated similarly. The volatile portion of the hydrolysis products (3·7 g.) consisted of aniline, whilst the alkaline residue yielded *p*-cresol (3·0 g.) and *p*-hydroxybenzoic acid (0·1 g.).

(V) *Action of Potassium Hydroxide on Dibenzylhydroxylamine.*—Dibenzylhydroxylamine (5 g.), prepared as described by Schramm (*Ber.*, 1883, **16**, 2104), was treated in the usual way, and the volatile products were isolated by distillation at 5 mm. Redistilled at 2 mm., these gave a small fraction (*a*) boiling up to 160°, and a main fraction (*b*), b. p. 160°. Fraction (*b*) consisted of benzylidenebenzylamine (Found: C, 85·8; H, 7·2. Calc.: C, 86·1; H, 6·7%), since on treatment with dilute hydrochloric acid it gave benzaldehyde (identified as its semicarbazone) and benzylamine (identified as hydrochloride). Fraction (*a*), although too small to purify, must

have contained much of the same azomethine, since the same amine and aldehyde were obtained from it.

We wish to thank the Chemical Society for a grant, with the aid of which part of the cost of this research has been met.

THE UNIVERSITY, LEEDS. [*Received, February 10th*, 1926.]

CLXIX.—*The Nature of the Alternating Effect in Carbon Chains. Part V. A Discussion of Aromatic Substitution with Special Reference to the Respective Rôles of Polar and Non-polar Dissociation ; and a further Study of the Relative Directive Efficiencies of Oxygen and Nitrogen.*

By CHRISTOPHER KELK INGOLD and EDITH HILDA INGOLD.

THE preceding parts of this series describe a partial examination of the theories of the alternating polarisation of atoms (A), and of the alternating affinity content of valencies (B), as applied to aromatic substitution :

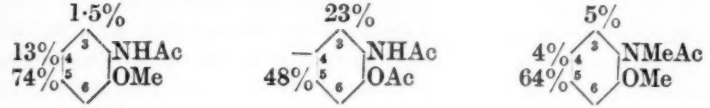
The criterion adopted was that, according to the first view, the more electronegative atoms of the series N, O, F, should produce the larger effects (F>O>N), whilst, according to the second, the reverse should hold, the most " unsaturated " atom being the most potent (N>O>F).

In Part III, a comparison of benzylamines and benzyl ethers was recorded, from which it was concluded that nitrogen is more effective than oxygen, which appeared to agree with theory (B). Observations have since been made, however, which show that even this theory is not adequate without extension, and that special factors must enter into the problem of the orientation of substances in which the " key-atom " is separated from the nucleus by a chain of one or more carbon atoms. It is therefore necessary to examine the application of other considerations. Nevertheless, the general conclusion previously reached with regard to the directive efficiencies of oxygen and nitrogen accords with that to which the present experiments on the nitration of derivatives of *o*-aminophenol have led.*

The results of these experiments are represented in the following

* The case of O versus F is dealt with in the following paper.

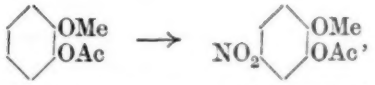
formulæ, in which the figures connote material accounted for in units per cent. of the theoretical :



(Total : 88%.) (I.) (Total : 71%.) (II.) (Total : 73%.) (III.)

It will be clear from these data that whether we disregard *o*-substitution as possibly subject to special influences and consider only substitution in positions 4 and 5, or whether we accept the total *op*-direction by each group as the best measure of its efficiency, the group containing nitrogen is the more effective, for (except in case II, in which the total recovery is not very satisfactory) more than 50% of the material was accounted for as the 5-nitro-derivative. Strictly speaking, these conclusions apply only to the cases dealt with, but it seems likely that they will hold fairly generally in the simpler analogous cases. Possible abnormality arising from indirect substitution *via* the amino-hydrogen atom is controlled by case (III), the results of which differ little from those of (I), and the differing effects of alkyl and acyl groups in modifying the directive efficiency of an oxygen or nitrogen atom are partly controlled by example (II). In any case, other data show that the distribution of alkyl and acyl groups in examples (I) and (III) is such as would handicap the nitrogen atom.

The depressing effect of acyl as compared with alkyl groups on *op*-directive power may be illustrated by the 4-nitration of acetylguaiacol,

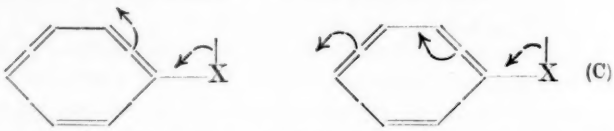


and is of importance in connexion with Smedley's formula for the carboxyl group (J., 1909, **95**, 231), a modernised interpretation of which would involve the recognition of a betaine-like phase,* the bond joining the oxygen atoms being an electrovalency. In the carboxylamide group, the nitrogen atom will necessarily constitute the positive end of the betaine linking, and thus forms arise which (on any theory, and by analogy also) would be expected to diminish the tendency towards *op*-substitution :

* Or a condition corresponding with partial conversion into such a phase.

The low value found by Sugden (J., 1924, **125**, 1185) for the parachor of the group CO_2 in carboxylic esters would then be attributed to shrinkage arising from electrostatic attraction.

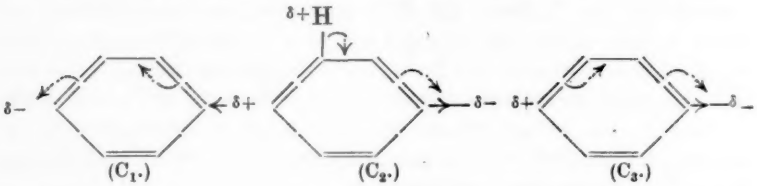
The above results, whilst they appear inconsistent with the idea of alternating polar charges (A), agree either with Flürscheim's theory of alternating affinity content (B), or with Robinson's theory (*Chem. and Ind.*, 1925, **44**, 456) of *op*-substitution by electronic displacement in conjugated systems (C).* This theory leads to much the same key-efficiency series as Flürscheim's, if residual affinity be interpreted as an indication of the presence of loosely held, active electrons. The arrows represent the assumed electron displacements originating in a latent valency:



(C)

It will be obvious that the distribution of forces here involved is qualitatively the same as that in Flürscheim's theory, the completed change (C) corresponding with his figure for *op*-substitution:

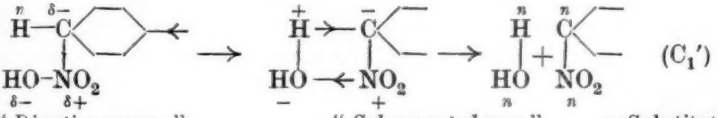
In applying these suggestive ideas to the cases of substitution previously described, we would regard the above formulæ as expressing only the direction of imaginary gross changes which actually do not at any time proceed to more than a limited (in some cases an exceedingly small) extent. This interpretation is placed upon the formulæ partly to cover the case of direction by methyl, which, we assume, has not electrons available for a complete co-valency change (even a momentary one), and is expressed by a slight change of symbolism (C_1),† the dotted arrows representing electronic strain:



* Since the above was written, a fuller statement has become available (this vol., p. 401).

† In this formula, and those which follow, δ+ and δ− are used to signify small fractions of a unit charge; *n* represents neutrality, and the signs + and − connote unit charges.

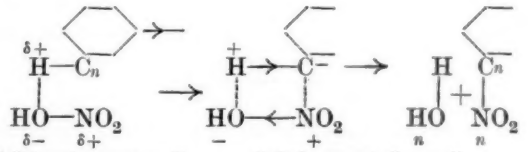
It may then be supposed that the *incipient* negative polarisation of the *o*- and *p*-carbon atoms (in different electromeric phases) would be sufficient to attract the positive end of an *incipiently* ionised molecule (*e.g.*, nitric acid or chlorine).* This corresponds with Flürscheim's theory of molecular addition at a point by *residual* (not real) valencies, and may be termed the "directive process." This having occurred, the tendency for hydrogen to unite *as a positive ion* (compare Part IV) with, for instance, hydroxyl or chlorine acting as a negative one, would lead to reaction in a four-cycle † (the "subsequent change") with the unit electron displacements shown, and without the necessity for any further electronic displacement in the benzene system itself:



(C$_1$′)

"*Directive process.*" "*Subsequent change.*" *op*-Substitution by positive groups.

The case of *m*-substitution is regarded as an effect produced by groups which tend to withdraw electrons from the nucleus (*loc. cit.*). Combining this suggestion with the evidence, discussed in Part IV, of incipiently ionised hydrogen in combination with carbon, and of its extraction in the form of a true ion by the hydroxyl ion, the view may be expressed (formula C$_2$) that the meta-hydrogen atom in these cases reaches a state of incipient ionisation, owing to a pull on the electrons involved in its linking with the nucleus. The meta-carbon remains approximately neutral, and the attack of an incipiently ionised reagent therefore begins at the positively polarised hydrogen atom: ‡



(C$_2$′)

"*Directive process.*" "*Subsequent change.*" *m*-Substitution by positive groups.

* Since ortho- *versus* para-substitution is not now under consideration, the operation of direct exchange with the *p*-position is disregarded to abbreviate description.

† Or, a third molecule might enter into the reaction, giving a six-cycle.

‡ The assumption of a less direct type of activation preceding *m*-substitution is consistent with the generally smaller velocities of these reactions as compared with *op*-substitutions.

Formula C_3 corresponds with the direction of negative ions to the *op*-positions (Robinson, *loc. cit.*) and need not be expanded, since the "subsequent change" may pursue different paths (leading to the same goal) according as the ionisation of the reagent is incipient, or actual * (hydrolysis of *p*-chloronitrobenzene).†

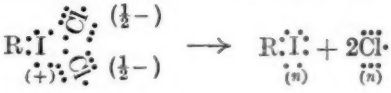
In applying these three principal directive effects, we bear in mind that they can determine only the (reversible) *initial attraction* of the reagent, and that the substitution cannot ensue unless the conditions necessary for the "subsequent change" are present. An essential condition in cases C_1 and C_2 is that the displaced atom should be one (*e.g.*, hydrogen) which tends to function as a *positive* ion, and can be extracted from the molecule as a positive ion under the conditions employed. Similarly, in C_3 the "subsequent change" can occur only if the expelled atom is one (*e.g.*, chlorine) which tends to function as a *negative* ion and is capable of being removed in this form by the reagent used. The importance of these auxiliary conditions may be illustrated by the fact that, neglecting them, C_3 necessitates that nitrobenzene and nitric acid should yield *p*-nitrophenol and nitrous acid, and many similar absurdities.

Taking count of "general" electronic restraint, subsidiary directive effects may be perceived which need not be stated. It has also to be remembered that the dissociation of a reagent into *neutral* atoms, or radicals, may lead to substitution in positions determined by the consideration that those neutral atoms (*e.g.*, Cl) which have to *gain* electrons to form their stable ions will seek out negative centres, and in this respect simulate a *positive* group, and *vice versa*. This may well be the mechanism of chlorination by phosphorus pentachloride, iodine trichloride and aryliodide di-

* In this case there can be no reaction in a cycle, and the "subsequent change" may involve a complete reversible conversion into the quinonoid condition.

† Whether a particular group will act as an "electron-source" or "electron sink" (this vol., p. 1307) towards the benzene ring is, in general, determined by the fact that electronic strain can in each case operate only in one way if all octets are to be preserved. Thus –OMe is necessarily a source, and –CH:O necessarily a sink so far as principal directive effects are concerned. Also, a fluorine atom directly attached to the ring can only act as a source by the mechanism considered, although in saturated chains it should act as a sink, tending towards separation as a negative ion (general polarity). For this reason, when directly joined to the nucleus, it acts as a source only with reluctance, *i.e.*, is only feebly *op*-directing (compare following paper). Direction by methyl and vinyl are special cases which do not appear to be capable of determination *a priori* by generally recognised electronic principles, although *experiment* indicates that each functions as a source in aromatic substitution.

chlorides, each of the two loosely-held chlorine atoms in these compounds being regarded as bound by a single electron (compare Prideaux, *Chem. and Ind.*, 1923, **42**, 672) and as in a state of incipient *atomic* dissociation of the following kind : *



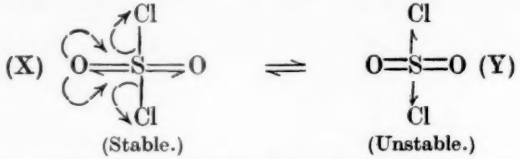
Again, the equation indicates only the direction, and not the extent, of the change (*i.e.*, dissociation) necessary to initiate reaction. Thus it happens that chlorine, although *negative* (0·5 unit charge) in the original group, tends to separate as a *neutral* atom which so desires an electron that it simulates a *positive* group. Thus the apparent anomaly of negative chlorine leaving positive iodine or phosphorus to become attached to negative carbon is explained. On this view, chlorination through the neutral atom can take place in system C_1, but not in C_2 or C_3, since only the first contains a negative centre; accordingly, phosphorus pentachloride readily chlorinates anisole in the *p*-position, but has no action on nitrobenzene.

The apparently anomalous introduction of the "negative" hydroxyl group into the *op*-positions of phenols, etc., in electrolytic oxidation is evidently an analogous phenomenon. If the substance oxidised is stable to alkalis (as is usually the case), the hydroxyl *ion* has, of course, no action; but when the anode strips an electron from it, it becomes a neutral free radical with a septet, and hence attacks the incipiently negative carbon atoms of the aromatic compound. Again, mechanism C_1 can function (*op*-substitution) but not C_2 (*m*-substitution), which corresponds precisely with ascertained fact : many electrolytic *op*-oxidations are on record, but, so far as we are aware, no *m*-oxidations.

Sulphuryl chloride may be regarded as having two electromeric forms, the stable one containing two semipolar double bonds (X), and the other only one semipolar double bond and two semipolar single bonds (Y). It is the latter which contains the labile chlorine, and it would be this form rather than the first which is concerned in chlorination by sulphuryl chloride. The action of this reagent is therefore not anomalous (compare Flürscheim, *Chem. and Ind.*,

* The small electrical conductivity of phosphorus pentachloride in nitrobenzene (Holroyd, Chadwick, and Mitchell, J., 1925, **127**, 2492) appears to favour this view, as against the ionic structure $(\overset{+}{PCl_4})\overset{-}{Cl}$. The bonds by which the labile chlorine atoms are held might be termed "semi-polar single bonds" and written $\rightharpoonup$ to avoid the use of signs such as $\frac{1}{2}+$ and $\frac{1}{2}-$.

1925, **44**, 172, 427; Robinson, *ibid.*, p. 259); it is another instance of attack by a neutral radical:



Thus, in conformity with the two known kinds of dissociation of co-valency compounds, it is suggested that both polar and non-polar dissociation may be concerned in aromatic substitution, the main determining condition being the electronic constitution of the reagent. This view, we think, interprets the data more consistently than is possible by means either of a purely ionic or of a purely non-ionic conception; it is advanced, however, mainly to facilitate discussion, for it is clear that the main principles, even if true, must be held as subject to possible modifications arising from other influences.

Experimental.

(I) *Nitration of Aceto-o-anisidide.*

Mulhauser (*Annalen*, 1899, **207**, 242) nitrated aceto-*o*-anisidide and obtained a mononitro-derivative, m. p. 143°. Meldola, Woolcott, and Wray (J., 1896, **69**, 1330) found m. p. 145—146°, and suggested that it was the 5-nitro-derivative (for numbering, see Formula I, p. 1311) but did not prove this orientation. The Fabrik de Produits Chimique de Thann et de Mulhause (D.R.-P. 98637) stated that the substance was in reality a mixture of two isomerides, m. p. 153° and 131—132° respectively. We find that, whilst the first of these is a pure compound, identical with 5-nitroaceto-*o*-anisidide synthesised by Vermeulen (*Rec. trav. chim.*, 1905, **25**, 12), the second is a mixture containing, besides the 5-nitro-compound, its 4-nitro-isomeride, m. p. 174—175°. Small quantities of the 3-nitro-compound, m. p. 158—159°, and, probably, of the 6-nitro-compound, m. p. 103—104°, are also produced in the nitration. The 4-nitro-compound was synthesised by Meldola, Woolcott, and Wray (*loc. cit.*) and by Vermeulen (*loc. cit.*). The properties of the 3- and 6-nitro-derivatives and their orientation are described below.

Qualitative Separations.—(I) A well-cooled solution of 1·5 c.c. of nitric acid (*d* 1·5) in 5 c.c. of acetic anhydride was added to the paste obtained by cooling a solution of 5 g. of acetanisidide in 10 c.c. of acetic anhydride to 0°. Heat was generated, but the temperature was not allowed to rise above 45°. The mixture was kept at the ordinary temperature for 24 hours and, after addition of water,

shaken to destroy acetic anhydride. The solid product (6·0 g.) was subjected to about 20 fractional crystallisations from absolute alcohol, which yielded the following apparently pure substances, here named in the order of their appearance: (*a*) large, stout, prisms, m. p. 153—154° (2·0 g.); (*b*) long, silky needles, m. p. 173·5—175° (0·1 g.); (*c*) rosettes of small needles, m. p. 129—131° (0·5 g.). By direct comparison (*a*) was shown to be 5-nitroaceto-*o*-anisidide, and (*b*) 4-nitroaceto-*o*-anisidide. The crystals (*c*) we assume to be identical with the product, m. p. 131—132°, described in D.R.-P. 98637, but direct comparison showed that it was neither 3-, 4-, 5-, nor 6-nitroaceto-*o*-anisidide. It had the correct composition (Found: C, 51·7; H, 4·9. $C_9H_{10}O_4N_2$ requires C, 51·4; H, 4·8%), and, since its m. p. was depressed by the addition of the 3- and 6-nitro-compounds and raised by the addition of either the 4- or the 5-derivative, we regard it as a difficultly separable mixture of the last two isomerides. After hydrolysis of the acetyl group, the corresponding free bases can be separated in the pure condition, the 5-derivative being isolated in larger quantity than the 4-isomeride.

(II) Another experiment using 40 g. of aceto-*o*-anisidide was carried out in the same way, excepting that the most soluble fractions obtained after a rough separation were combined with the product isolated by neutralising the dilute acetic acid solution and extraction with ether, and fractionally crystallised as completely as possible. Fractions identical with (*a*) and (*c*) were obtained, and also a very small amount of a substance, m. p. 99—103°, which did not depress the m. p. (103—104°) of synthetic 6-nitroaceto-*o*-anisidide, but was insufficient for analysis.

Further experiments did not lead to the isolation of the 3-isomeride, although the presence of this was proved indirectly.

3-*Nitroaceto*-o-*anisidide*.—3-Nitro-*ON*-diacetyl-*o*-aminophenol (see below) (0·5 g.) was treated at 30—40° with 2 c.c. of cold 2*N*-sodium hydroxide and the deep red solution was shaken with successive small quantities of methyl sulphate, additional alkali being added as it became necessary. When the red colour had given place to lemon-yellow, the precipitate was collected and crystallised from alcohol; pale yellow needles, m. p. 158—159°, were then obtained (Found: C, 51·7; H, 4·8. $C_9H_{10}O_4N_2$ requires C, 51·4; H, 4·8%). The m. p. of this substance was depressed 20° to 60° by the addition of its isomerides, 4-, 5-, and 6-nitroaceto-*o*-anisidide. Since the 4-, 5-, and 6-compounds were all synthesised by methods which showed their constitutions, the orientation of the 3-derivative follows. It was confirmed by conversion of the substance into 3-nitroguaiacol by boiling for 36 hours with 2*N*-sodium hydroxide

and acidifying the resulting solution. This guaiacol was not synthesised for comparison, but the specimen obtained had the m. p. (60—61°) and properties recorded in the literature, and had the large volatility with steam characteristic of *o*-nitrophenols (see below). The base, 3-*nitro*-o-*anisidine*, was obtained by heating the acetyl derivative for 30 minutes with 20% hydrochloric acid on the steam-bath and extracting the product with ether from the solution basified with ammonia. The same base was obtained along with 3-nitroguaiacol when the acetyl compound was boiled for 6 hours with 2*N*-aqueous sodium hydroxide. It separated from alcohol in bright scarlet needles, m. p. 75—76° (Found: C, 50·0; H, 4·8. $C_7H_8O_3N_2$ requires C, 50·0; H, 4·8%).

4-*Nitroaceto*-o-*anisidide*.—This was prepared by Meldola, Woolcott, and Wray's method (*loc. cit.*). It had m. p. 174—175°, and the corresponding free base, m. p. 117—118°. On boiling either the base or its acetyl derivative for 30 hours with 2*N*-aqueous sodium hydroxide under the conditions in which the 3- and 5-isomerides yield nitroguaiacols, deep-seated decomposition took place, although some unchanged base was recovered. A specimen of 4-nitroguaiacol, m. p. 103—104°, was prepared by the direct nitration of acetylguaiacol (Reverdin and Crepieux, *Ber.*, 1903, **36**, 2258; 1906, **39**, 4232; Paul, *Ber.*, 1906, **39**, 2779) but, even on seeding with a crystal of this, the same compound could not be obtained from the small quantity of acidic tar isolated from the product of hydrolysis. A few crystals, m. p. 80—90°, were obtained, but the amount was insufficient for purification.

5-*Nitroaceto*-o-*anisidide*.—Vermeulen's method (*loc. cit.*) was used for the preparation of this substance, which was obtained in large, pale yellow, nearly cubical prisms, m. p. 153—154°. On cooling a solution of it in warm concentrated hydrochloric acid, a sandy precipitate was obtained, which on treatment with water turned yellow. Its solution in much boiling water was rendered alkaline with sodium carbonate and cooled; the free base then separated as golden-yellow, flattened needles, m. p. 139—140°. On boiling for 36 hours with 2*N*-aqueous sodium hydroxide, either the acetyl derivative or the base is converted fairly smoothly into 5-nitroguaiacol, which is precipitated on acidification, the filtrate containing a further quantity isolable by extraction with ether. This nitroguaiacol had m. p. 99—100° and depressed the m. p. of 4-nitroguaiacol.

6-*Nitroaceto*-o-*anisidide* was synthesised from 2 : 6-dinitroanisole by partial reduction and acetylation of the nitro-base. An alcoholic solution of 2 : 6-dinitroanisole was treated for 30 minutes with a rapid stream of hydrogen sulphide. During the first 10 minutes

much heat was developed. Water was added, and the base extracted from the precipitate by digestion with 20% hydrochloric acid, from which it was reprecipitated on addition of ammonia. Having been dried as rapidly as possible, the crude base was repeatedly extracted with boiling ligroin until the extracts failed to crystallise on cooling. 6-*Nitro*-o-*anisidine* was thus obtained as bright yellow, flattened needles, m. p. 65—66°, a further quantity being recoverable from the ligroin solution. An additional crystallisation from ligroin raised the m. p. to 67° (Found : C, 50·0; H, 4·7. $C_7H_8O_3N_2$ requires C, 50·0; H, 4·8%). The *acetyl* derivative was obtained by boiling the base for 2 hours with acetic anhydride, and crystallised from methyl alcohol or dilute acetic acid in pale yellow prisms, m. p. 103—104° (Found : C, 51·5; H, 4·8. $C_9H_{10}O_4N_2$ requires C, 51·4; H, 4·8%). Attempts to convert either of these substances into 6-nitroguaiacol by the method used for the corresponding reaction in the 5-series led to deep-seated decomposition and products from which no crystalline substance could be isolated.

Attempted Estimation of the Proportions of the Isomerides.—(i) The nitration of 40 g. of aceto-*o*-anisidide was carried out in acetic anhydride as described above and the product allowed to crystallise over-night, when 9·1 g. of the 5-nitro-compound separated. The acetic anhydride was then removed by desiccation at a low pressure over potassium hydroxide. The residue was fractionally crystallised from alcohol, and a further quantity of 5-nitro-compound (1·5 g.) and some 4-nitro-compound (1·0 g.) were obtained. The weights are those of the fully purified isomerides. The unseparated residue was hydrolysed with hydrochloric acid and the bases were fractionated from alcohol, the 5-nitro-base (3·7 g.) and the 4-nitro-base (0·65 g.) being isolated. The unseparated portions were reacetylated and by further crystallisation the 5-nitro-acetyl derivative (2·1 g.) and its 4-isomeride (1·4 g.) were obtained. About 1 g. of a mixture remained which was not resolved. The total pure substances isolated corresponded with 68% of 5-nitro-compound and 13% of 4-nitro-compound.

(ii) In a similar experiment to the above, 37% of 5-nitroaceto-*o*-anisidide separated from the acetic anhydride. The residue obtained on complete evaporation was boiled for 36 hours with 10 times its weight of 2*N*-sodium hydroxide, and the resulting solution diluted to dissolve the red, rather sparingly soluble sodium salt of 5-nitroguaiacol, and extracted with ether. The bases thus recovered (2·8 g., and in another similar experiment 3·5 g.) were contaminated with products of deep-seated decomposition, but yielded some crystalline 4-nitroanisidine. On acidification of the alkaline solution 5-nitroguaiacol (11·2 g.), m. p. 96—99°, was obtained, and the

mother-liquors yielded a mixture of guaiacols, which were recovered by extraction with ether and purified and partly separated by distillation in steam. Experiments with artificial mixtures of 3-nitroguaiacol and 5-nitroguaiacol showed that the former passed over completely in the early stages of distillation, but that a small quantity of the latter was present in all fractions. Further experiments to determine the volatility of 5-nitroguaiacol in steam indicated that, under the usual conditions of distillation, the steam reaching the condenser is not quite saturated; but by working under uniform conditions as regards apparatus and rate of distillation a fairly consistent figure of 1·20 g. per litre was obtained and this was regarded as sufficiently accurate in experiments carried out under like conditions. In the distillation of the mixed guaiacols described above, the first 500 c.c. of distillate yielded 1·26 g., m. p. 60—80°, whilst the succeeding 500 c.c. fractions each gave 0·6 g., m. p. 97—100°, so that 0·66 g. of the more volatile 3-nitroguaiacol was assumed to be present in the original mixture. This corresponded with a yield of 1·5%, whilst the total quantity of 5-nitroguaiacol was equivalent to 37% of the theoretical, a further 37% of 5-nitroaceto-*o*-anisidine having been also obtained as described above.

Combining these results, it follows that in the original nitrations the 5-nitro-derivative was formed to the extent of at least 74%, the 4-nitro-compound to the extent of at least 13% and the 3-isomeride to the extent of about 1·5%, a small quantity of the 6-compound probably also being produced. The total yield was 88·5%.

(II) *Nitration of* ON-*Diacetyl-o-aminophenol.*

The nitration of *ON*-diacetyl-*o*-aminophenol was carried out by Meldola, Woolcott, and Wray (*loc. cit.*), who isolated the 5-nitro-derivative, m. p. 189°, which they definitely oriented. They did not notice the formation of a second isomeride. Our attempts to follow their method yielded either dinitro-compound, or mixtures of unchanged material with mono- and di-nitro-derivatives. On the other hand, treatment with the theoretical quantity of nitric acid in warm acetic anhydride led to smooth mononitration.

Dinitration.—A solution of the diacetyl compound (10 g.) in a mixture of 40 c.c. of ordinary concentrated nitric acid and 20 c.c. of fuming acid at −5° was kept for 2 hours at 2—4°, and ice then added. The precipitate, which was collected on the next day, crystallised from boiling water in long, yellow needles, m. p. 202°. Since analysis (Found: C, 40·2,; H, 3·2; N, 17·8. $C_8H_7O_6N_3$ requires C, 39·8; H, 2·9; N, 17·5%) indicated that one acetyl group had been eliminated, and the substance gave an immediate

precipitate of the red potassium salt when treated in alcoholic suspension with cold dilute potassium hydroxide solution, we regard it as 3 : 5-*dinitro*-N-*acetyl*-o-*aminophenol*. The compound was not definitely oriented, but the positions of the nitro-groups are inferred from the study of the mononitration of diacetylaminophenol described below.

Mononitration. Qualitative Separation of Isomerides.—The paste obtained by cooling a solution of diacetyl-*o*-aminophenol (20 g.) in acetic anhydride (40 g.) to 15° was treated gradually with an ice-cold mixture of 5 c.c. of nitric acid (*d* 1·5) and 20 c.c. of acetic anhydride. The crystals dissolved and the temperature rose rapidly, but was kept from exceeding 35° by external cooling. When self-heating had ceased, the mixture was allowed to cool to the ordinary temperature; a stiff paste of yellow crystals then formed. Several hours later, the acetic anhydride was destroyed by shaking with water, and the solid product, m. p. 140—160°, collected. This was fractionally extracted with boiling alcohol; the less soluble product, m. p. 165—180°, thus obtained, after four crystallisations from alcohol, yielded very characteristic, long, pale yellow needles, resembling glass wool, the m. p., 189°, of which was not further changed by crystallisation. The more soluble fractions were subjected to a prolonged series of fractional crystallisations from alcohol, when stout, pale yellow tablets, m. p. 183°, were obtained. The isolation of these was facilitated by the observation that, after slow crystallisation, they could be partly separated from the filamental needles by shaking and rapidly decanting the mother-liquor, but the process was slow, and after about 40 crystallisations, only 6·0 g. of the needles, m. p. 189°, and 3·1 g. of the tablets, m. p. 183°, had been obtained. Needles, m. p. about 160°, were also obtained, but these appeared to be a difficultly separable mixture of which the needles, m. p. 189°, formed one constituent.

3-*Nitro*-ON-*diacetyl*-o-*aminophenol*.—This constitution is assigned to the tablets, m. p. 183° (Found : C, 50·3; H, 4·1. $C_{10}H_{10}O_5N_2$ requires C, 50·4; H, 4·2%), since the corresponding free phenol is converted by methylation into 3-nitroaceto-*o*-anisidide, the orientation of which is described above. 3-*Nitro*-o-*acetylaminophenol* was formed as its sodium salt when the acetyl compound (0·5 g.) was treated with 2 c.c. of 2*N*-aqueous sodium hydroxide. The temperature rose to 40° and the solid dissolved, but the deep red solution did not crystallise. The phenol was precipitated on acidification and crystallised from hot water in orange-yellow needles, m. p. 169°.

4-*Nitro*-ON-*diacetyl*-o-*aminophenol*.—4-Nitro-*o*-aminophenol (3 g., obtained by reduction of 2 : 4-dinitrophenol with hydrogen sulphide)

was boiled with acetic anhydride (4·5 g.) and acetic acid (2 g.) for 2 hours. The excess of acetic acid was removed over potassium hydroxide in an evacuated desiccator, and the solid product drained on porous porcelain and crystallised twice from ethyl alcohol, when needles, m. p. 183—184°, were obtained (Found : C, 50·2; H, 4·2. $C_{10}H_{10}O_5N_2$ requires C, 50·4; H, 4·2%). *4-Nitro-*o*-acetylaminophenol* was prepared as in the preceding series, but it yielded an orange sodium salt which separated from the alkaline solution in rosettes of needles. The free phenol crystallised from alcohol in colourless prisms, m. p. 278° (decomp.) (Found : C, 48·8; H, 4·1. $C_8H_8O_4N_2$ requires C, 49·0; H, 4·1%).

*5-Nitro-*ON*-diacetyl-*o*-aminophenol.*—This structure is assigned to the filamental needles, m. p. 189°, obtained by nitration, since the corresponding phenol on methylation gave 5-nitroaceto-*o*-anisidide. *5-Nitro-*o*-acetylaminophenol* was prepared as in the last case. Crimson needles separated from the alkaline solution, which, on addition of water and acid, yielded the phenol. After crystallisation from ethyl alcohol, this was obtained in small, yellow prisms, m. p. 269° (decomp.) (Found : C, 48·8; H, 4·1. $C_8H_8O_4N_2$ requires C, 49·0; H, 4·0%).

Attempted Estimation of the Proportions of 3- and 5-Nitro-derivatives.—The nitration of diacetylaminophenol (40 g.) was carried out as described above, and the acetic anhydride removed in a vacuum, without separation of the part of the nitration product which crystallised spontaneously, since this was a mixture of isomerides. The solid residue was mixed with 120 c.c. of water and 180 c.c. of 4*N*-aqueous potassium hydroxide, the temperature being kept below 35°. When the decomposition (elimination of the *O*-acetyl group) was completed, the deep red liquid was acidified and the precipitated phenols were collected; a small additional quantity of solid was obtained by extracting the mother-liquor with ether. The whole solid was then mixed with 100 c.c. of 2*N*-potassium hydroxide and shaken at 25—35° with 10 c.c. of methyl sulphate. The methylation was almost complete in an hour, and was finished with the aid of small additional amounts of methyl sulphate and alkali. The precipitated solid was washed with water, boiled for 36 hours with 400 c.c. of 2*N*-aqueous potassium hydroxide (ammonia ceased to be evolved after the first 24 hours), and the cooled product extracted with ether to remove unchanged bases, and basic tars (7·0 g.). After the dissolved ether had been removed in a current of air, the solution was acidified. The mixed guaiacols thus precipitated were kept in contact with the mother-liquor for 24 hours to become thoroughly crystalline, and then collected, the dissolved portions being isolated by extraction with ether (total 25 g.). They

were separated and estimated by steam distillation, as described in the previous example. In this case, owing to the relatively large proportion in which it was present, the *O*-compound crystallised (5·8 g.) in a pure form (orange needles, m. p. 60—61°) from the first 2 l. of distillate. A further 2·2 g. was estimated to be present in solution in the first 3 l. of distillate, by extracting it with pure ether and correcting for the volatility in steam of the *p*-compound with which it was contaminated. Of this 2·2 g., about 1·1 g. were separated in the pure condition by fractional crystallisation from water. The distillate following the first 3 l. contained only the *p*-compound which, without crystallisation, melted at 96—99° and, after crystallisation, at 99—100°. These yields correspond with 23% of 3-nitrodiacetylaminophenol and 48% of the 5-nitro-compound. No solid product could be isolated from the tarry basic fraction, so the quantity of 4- and 6-derivatives formed is left undetermined.

(III) *Nitration of* N-*Methylaceto*-o-*Anisidide.*

N-Methyl-*o*-anisidine was prepared by methylating the formyl derivative of *o*-anisidine and, after hydrolysis of the formyl group, was isolated by means of the nitrosoamine, which was reduced to the secondary base as described by Diepolder (*Ber.*, 1899, **32,** 3515).

N-*Methylaceto*-o-*anisidide* was prepared by boiling the base for 2 hours with a slight excess of acetic anhydride and distilling the product. The fraction, b. p. 158—160°, set on cooling to a mass of large, inclined prisms, m. p. 46—50°, which, after crystallisation from ether–ligroin, melted at 51—53° (Found: C, 67·4; H, 7·3. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3%).

Mononitration: Isolation of 5-*Nitro-*, 4-*Nitro-*, *and* 3- *or* 6-*Nitro-derivatives.*—A cooled mixture of fuming nitric acid (2·5 c.c.) and acetic anhydride (12 c.c.) was added to *N*-methylaceto-*o*-anisidide (10 g.) dissolved in acetic anhydride (24 c.c.), the temperature being kept below 35°. Two methods of isolating the crude nitration product were employed. (i) The solution was poured into water, shaken to decompose the acetic anhydride, and made alkaline with sodium carbonate. Any solid which separated was collected, and the filtrate extracted with ether. The extract was dried with calcium chloride and reduced by evaporation to a small bulk, the crystals being separated fractionally. (ii) The acetic anhydride was removed by evaporation in a vacuum over potassium hydroxide.

Methylaceto-*o*-anisidide (20 g.) on nitration, followed by treatment in accordance with method (i), yielded 12·5 g. of a crystalline solid, m. p. 117—119°, which on crystallisation from ether formed

pale yellow prisms, m. p. 119—120·5°. This was shown to be 5-*nitro*-N-*methylaceto*-o-*anisidide* by direct comparison with a specimen synthesised as described below (Found: C, 53·8; H. 5·4. $C_{10}H_{12}O_4N_2$ requires C, 53·6; H, 5·4%).

On evaporating the ethereal extract to small bulk, very pale yellow prisms, m. p. 120—125°, which depressed the m. p. of the 5-nitro-compound, separated (0·9 g.). On crystallisation from benzene–ligroin the m. p. was raised to 126·5—127·5°. This substance was identified as 4-*nitro*-N-*methylaceto*-o-*anisidide* by comparison with a specimen synthesised as described below (Found: C, 53·8; H, 5·4; N, 12·7. $C_{10}H_{12}O_4N_2$ requires C, 53·6; H, 5·4; N, 12·5%).

The ethereal solution from which this had separated, on cooling to −15°, deposited crystals (1·6 g.), m. p. 98—99°, from which 0·65 g. of pure 5-nitro-compound was separated by fractional crystallisation. The second substance present in this fraction could not be definitely identified.

On long standing, the residual ethereal solution deposited large, colourless prisms, m. p. 103—105°, which after crystallisation from ether melted at 105—106° (0·08 g.). This m. p. was not changed by further crystallisation (Found: C, 53·6; H, 5·3. $C_{10}H_{12}O_4N_2$ requires C, 53·6; H, 5·4%). We believe this substance to be 3-*nitro*-N-*methylaceto*-o-*anisidide*, which is certainly formed in the nitration (see below), but there is no definite proof that it is not the 6-nitro-isomeride. A further quantity of these crystals (0·16 g.) separated after a few weeks, but the remainder of the nitration product refused to crystallise. The compound, m. p. 105—106°, yielded on hydrolysis a *base* melting at about the ordinary temperature, but the quantity obtained was too small for purification. In another nitration carried out as far as possible under similar conditions, none of the above nitro-compound was isolated, only the 4-derivative, m. p. 126·5—127·5°, being obtained on cooling the ethereal solution to −20°.

Preliminary experiments having shown that 5-nitro-*N*-methylaceto-*o*-anisidide only slowly evolves methylamine on boiling with 2*N*-alkali, but that this reaction occurs at 120° in sealed tubes (although not so smoothly as the analogous reaction described previously), the presence of 3-nitro-*N*-methylaceto-*o*-anisidide was proved by the following experiment. *N*-Methylaceto-*o*-anisidide (7·3 g.) was nitrated in the usual way, and the product treated in accordance with method (ii). The crude product (8·7 g.; theory 9·0 g.) having partly crystallised (4·3 g. of the 5-nitro-derivative), a portion (3·4 g.) of the mechanically separated oil was heated with 30 c.c. of 2*N*-aqueous potassium hydroxide for 12·5 hours at 120°.

After extraction of the basic portion * (1·0 g.) with ether, the solution was acidified and the guaiacols (1·8 g.) were extracted. Fractional distillation in steam indicated the presence of 0·29 g. of 3-nitroguaiacol, and a small portion of this was obtained from the early fractions of the steam distillate; after crystallisation from water, it was identified by comparison and a mixed m. p. determination with the specimen obtained as described previously.

5-*Nitro*-N-*methyl*-o-*anisidine*.—The acetyl derivative (above) (0·9 g.) was heated with concentrated hydrochloric acid for 1·5 hours on the steam-bath, and the reaction completed by boiling for 45 minutes. Neutralisation with ammonia precipitated the base, which separated from methyl alcohol or light petroleum in long, bright yellow, flattened needles, m. p. 101—102°. It was identified as 5-nitro-*N*-methyl-*o*-anisidine by comparison with a specimen prepared by synthesis (below) (Found : C, 52·6; H, 5·4. $C_8H_{10}O_3N$ requires C, 52·7; H, 5·5%).

4-*Nitro*-N-*methyl*-o-*anisidine*.—Prepared in the same way from its acetyl derivative (above), this base separated from light petroleum in orange, hair-like crystals, m. p. 87°, which were identified by comparison with a synthesised specimen (below) (Found : C, 52·6; H, 5·5. $C_8H_{10}O_3N_2$ requires C, 52·7; H, 5·5%).

Synthesis of 5-*Nitro*-N-*methyl*-o-*anisidine*.—5-Nitroanisidine (1 g.), methyl iodide (0·9 g.), and methyl alcohol (2 c.c.) were heated together for 1·5 hours at 100° in a sealed tube. The alcohol was then evaporated, and dilute potassium hydroxide was added to precipitate the bases which, after partial purification with chloroform, yielded the secondary base on crystallisation from dilute methyl alcohol and from light petroleum.

Synthesis of 4-*Nitro*-N-*methylaceto*-o-*anisidide and* 4-*Nitro*-NN-*dimethyl*-o-*anisidine*, 4-*Nitro*-N-*methyl*-o-*anisidine, and* 4-*Nitro*-3(or 5)-*methylaceto*-o-*anisidide*.—4-Nitroanisidine (6 g.), methyl iodide (5·4 g.), and methyl alcohol (12 c.c.) were heated for 2 hours at 100°, and the mixture of bases was isolated, as in the previous preparation. Many attempts were made to separate these by fractional crystallisation, but without success, and the mixture was therefore heated with acetic anhydride for 45 hours. After the excess of this reagent had been evaporated, water was added and the mixture made alkaline with sodium carbonate and extracted with ether, the extract

* As in the two cases previously described, the bases recovered after alkali treatment contained products of some more complex change than the mere elimination of an acetyl group from the 4- or 6-nitro-derivative. In this experiment, the basic fraction, even after distillation and attempted acetylation, yielded liquids which could not be crystallised and the nature of which was not revealed by analysis.

being washed with 15% hydrochloric acid. This was intended to remove the tertiary base from the mixture of acetyl compounds of the primary and secondary bases, and in the earlier experiments by this method 4-*nitro*-NN-*dimethyl*-o-*anisidine* was isolated in this way, the material obtained by basifying the hydrochloric acid solution and extraction with ether setting to a solid mass, which, on crystallisation from ligroin, yielded bright yellow, short needles, m. p. 38—39·5° (Found: C, 54·7; H, 6·0. $C_9H_{12}O_3N_2$ requires C, 55·1; H, 6·1%).

In certain subsequent experiments, carried out as far as possible under the same conditions, the bases obtained from the hydrochloric acid extract did not solidify immediately, but on keeping for several weeks in an evacuated desiccator, partly crystallised. The crystals thus obtained separated from benzene–ligroin in very pale yellow prisms, m. p. 127—128°, which did not depress the m. p. of the specimen of 4-*nitro*-N-*methylaceto*-o-*anisidide* obtained by nitration. On hydrolysis with hydrochloric acid, the substance yielded 4-*nitro*-N-*methyl*-o-*anisidine*, m. p. 87°, which was similarly identified with the base prepared from the 4-nitration product. As an isomeric base, in which the methyl group has apparently migrated to the ring, was also isolated in the course of these experiments (see below), the secondary character of this base, m. p. 87°, was confirmed by the preparation of its *nitrosoamine*, which was precipitated at once when sodium nitrite was added to a solution of the hydrochloride. Crystallised from benzene–ligroin, this compound formed very pale yellow needles, m. p. 119—120° (Found: N, 20·3. $C_8H_9O_4N_3$ requires N, 19·9%). From these experiments, it must be concluded that 4-nitro-*N*-methylaceto-*o*-anisidide is fairly easily soluble in hydrochloric acid of the strength used. The oil from which the crystals of this compound were obtained set, some weeks later, to a solid mass consisting principally of the tertiary base described above.

The ethereal solution from which the above-mentioned substances were extracted by hydrochloric acid, on evaporation, yielded a solid residue which examination with a lens showed to contain at least two compounds. One of these was easily separated by fractional crystallisation and proved to be the acetyl derivative of the original primary base. The second compound was separated partly by crystallisation and partly mechanically, and, after a final crystallisation from benzene–ligroin, was obtained as pearly plates, m. p. 127—128°. It therefore had the same m. p. as 4-nitro-*N*-methylaceto-*o*-anisidide, but its crystalline form was entirely different, and a mixture of the two compounds melted at about 100°. Analysis showed the new compound to be an isomeride (Found: C, 53·2; H, 5·1; N, 12·2. $C_{10}H_{12}O_4N_2$ requires C, 53·6; H, 5·4; N, 12·5%),

and it must therefore be 4-*nitro*-3(or 5)-*methylaceto*-o-*anisidide*, a methyl group having wandered to the ring. To confirm this, the compound was boiled with hydrochloric acid for 0·5 hour to eliminate the acetyl group, and the hydrochloride of the base diazotised in the usual way. No precipitate separated, indicating that secondary bases were absent, but on pouring the product into alkaline β-naphthol solution, a deep crimson dye was immediately precipitated.

Action of Methyl Iodide on 6-*Nitro*-o-*anisidine*.—The base (2·2 g.), methyl iodide (2·0 g.), and methyl alcohol (4·5 c.c.) were heated together, and the products treated as in the methylation of 4-nitroanisidine. The mixture of acetyl compounds only partly solidified after long keeping. After several crystallisations from ether, colourless prisms were obtained, m. p. 106—107°, which depressed the m. p., 103—104°, of 6-nitroaceto-*o*-anisidide (Found: C, 52·7; H, 5·2. $C_8H_{10}O_3N_2$ requires C, 52·7; H, 5·5%). These analytical figures agree moderately well with those required for a nitromethylanisidine, but as the crystals were colourless, whilst the nitromethylanisidines described above are orange or yellow, it seems unlikely that this compound is a nitro-base of the series. Owing to the limited quantity of 6-nitro-*o*-anisidine available, we were not able to make a more detailed study of its methylation products, or to carry out further experiments with the substance described.

Attempted Estimation of the Proportions of the Nitration Products.—(*a*) *N*-Methylaceto-*o*-anisidide (20 g.), nitrated as described above and treated by method (ii), gave 11·8 g. of crystalline 5-nitro-derivative and 12·0 g. of an oily mixture (total 23·8 g.; theory 25·0 g.). A part of the oil (9·3 g.) gave guaiacols consisting, as estimated from fractional distillation in steam, of 3·3 g. of 5-nitro- and 1·0 g. of 3-nitro-guaiacol. A basic oil (2·7 g.) and a neutral tar (1·0 g.) were also obtained.

(*b*) In another experiment, 20 g. of *N*-methylaceto-*o*-anisidide yielded 14·0 g. of the 5-nitro-derivative and 0·9 g. of the 4-nitro-derivative, both isolated as such in the pure condition. In another experiment, in which the material was treated by method (i), similar quantities of the 5- and 4-nitro-compounds were isolated, and also 0·24 g. of an isomeride believed to be the 3-nitro-derivative.

Combining these results, 73% of the material is accounted for as follows: 5-nitro-derivative, 64%; 4-nitro-derivative, 4%; 3-nitro-derivative, 5%.

Addendum. ON-*Diacetyl*-N-*methyl*-o-*aminophenol*.—*N*-Methyl-*o*-aminophenol, which we found to melt at 88° instead of 80° as recorded in the literature, (44 g.) was boiled for 1 hour with acetic anhydride (70 c.c.), and the product distilled. The fraction, b. p. 160—170°/2 mm., at once solidified to crystals (61 g., m. p. 58—60°) which, after

crystallisation from ether–ligroin, had m. p. 63—64° (Found: C, 64·0; H, 6·2. $C_{11}H_{13}O_3N$ requires C, 63·8; H, 6·3%).

Originally it was intended to include a study of the nitration of this substance in this investigation, but this project was abandoned when it was found that a considerable amount of oxidation took place under the conditions which had been used for the mononitration of the other three substances.

We wish to thank the Royal Society for a grant with the aid of which part of the expense of this investigation has been met.

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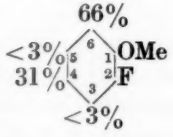
CLXX.—*The Nature of the Alternating Effect in Carbon Chains. Part VI. A Study of the Relative Directive Efficiencies of Oxygen and Fluorine in Aromatic Substitution.*

By ERIC LEIGHTON HOLMES and CHRISTOPHER KELK INGOLD.

IN continuation of the work, described in the preceding part, on the establishment of the sequence N>O>F for the *op*-directive powers of these atoms in the neutral state and directly attached to the benzene ring, the method previously used for comparing the relative directive efficiencies of nitrogen and oxygen atoms has now been applied to the comparison of oxygen with fluorine. *o*-Fluoroanisole has been nitrated with the results indicated in the following formula:



The methods by which these figures have been determined are fully described in the experimental portion, and it need only be stated here that the 3- and 5-nitro-derivatives were estimated together (2·7%) by taking advantage of the lability of their fluorine towards alkaline reagents, and that the 4-nitro-compound was estimated colorimetrically after reduction, utilising the fact that *p*-anisidine gives a violet coloration with ferric chloride, whilst the *o*-compound does not. The 4-nitro-derivative was isolated as such from the nitration mixture and identified by synthesis, whilst the 6-nitro-compound, which was also synthesised and was a liquid at

the ordinary temperature, was reduced with elimination of fluorine and identified as *o*-anisidine hydrochloride.

From the data given, it is clear that whether we disregard the large amount of *o*-substitution as an effect to which special influences contribute and consider only substitution in positions 4 and 5, or whether we accept the total *op*-direction by each group as the better measure of its directive power, the oxygen atom is the more effective directing agent. So great is the difference that although only one case has been investigated it appears reasonable to infer that the conclusion drawn will hold generally amongst derivatives of *o*-fluorophenol.

The sequence N>O>F is thus established; and this is the expected sequence, since the electronic grouping of fluorine most closely approaches the internally satisfied condition exemplified in neon (preceding paper).

Experimental.

Preparation of o-*Fluoroanisole.*—Some difficulty was experienced in obtaining this substance, but it was ultimately prepared by the action of hydrofluoric acid on the *diazopiperidide* obtained from *o*-anisidine. A solution of 25 g. of *o*-anisidine in 60 c.c. of hydrochloric acid was diazotised below 0° by a solution of 15 g. of sodium nitrite in 50 c.c. of water, the mixture being mechanically stirred. On pouring the product into a solution of potassium hydroxide (30 g.) and piperidine (17 g.) in 150 c.c. of water, an oil was precipitated which rapidly solidified (yield 35—37 g.) and on crystallisation from methyl alcohol yielded lemon-yellow prisms, m. p. 30° (Found: C, 65·0; * H, 7.6. $C_{12}H_{17}ON_3$ requires C, 65·8; H, 7·8%).

This diazopiperidide (35 g.) was heated for 1 hour on the steam-bath with 150 c.c. of concentrated aqueous hydrofluoric acid. Ice was then added and the mixture poured into an excess of 30% aqueous sodium hydroxide, care being taken to avoid over-heating, since the fluoroanisole is very volatile with steam. The *fluoroanisole* was isolated by distillation in steam and separated from the piperidine contained in the steam-distillate by extraction with ether after acidification. It is a colourless, mobile liquid, b. p. 154—155° (Found: C, 66·6; H, 5·6. C_7H_7OF requires C, 66·7; H, 5·6%). The average yield was 6% of the theoretical.

Dinitration.—In a preliminary experiment in which 1 g. of *o*-fluoroanisole was run through a fine capillary tube into 2 c.c. of

* A better analysis is, unfortunately, not available; difficulty was experienced in burning the substance owing to the rapidity with which it decomposed.

nitric acid (*d* 1·5) at −10°, and the product mixed with crushed ice, a solid dinitro-compound was obtained which on crystallisation from ethyl alcohol formed pale yellow needles, m. p. 86—87°. Judging from the results of mononitration (below), we believe this to be 4 : 6-*dinitro*-2-*fluoroanisole*, although no special proof of its constitution is here offered (Found : C, 38·7; H, 2·2. $C_7H_5O_5N_2F$ requires C, 38·9; H, 2·3%).

Mononitration.—*o*-Fluoroanisole (6·5 g.), mixed with acetic anhydride (25 g.), was treated at 0° with a mixture of fuming nitric acid (2·20 c.c.) and acetic anhydride (9 c.c.). The nitration proceeded smoothly with evolution of heat, and the mixture was kept at the ordinary temperature for 3—4 hours and then poured into water. The oil which separated was collected and diluted with ether, the aqueous solution was extracted with ether, and the combined ethereal solutions were dried and evaporated. The residue, after drying for a short time over potassium hydroxide, was distilled, practically the whole boiling at 114—116°/2 mm. (Found : C, 49·2; H, 3·4. $C_7H_6O_3NF$ requires C, 49·1; H, 3·5%).

3-*Nitro- and* 5-*Nitro*-o-*fluoroanisole.*—These were estimated together by taking advantage of the lability of their fluorine in the presence of boiling 0·5*N*-aqueous sodium carbonate, or dilute methyl-alcoholic sodium methoxide prepared from 2 g. of sodium and 200 c.c. of methyl alcohol. With the first of these reagents at its boiling point, and with the second at 60°, a quantity of fluoride ion corresponding with the decomposition of about 2·5—3·0% of nitrofluoroanisole was liberated rapidly, whilst prolonged treatment produced very little further action. After 3 hours' treatment with boiling sodium carbonate, the liberation of fluoride ion corresponded to 2·7% of decomposed nitrofluoroanisole (average of three concordant determinations) and almost the same figure, 2·8%, was obtained on using sodium methoxide. To ascertain if any correction was needed for the possible decomposition of the 4- and 6-nitro-derivatives, these two substances (see below) were treated for the same period under the same conditions. With 4-nitrofluoroanisole and sodium carbonate, the decomposition was zero (two determinations), and the same result was obtained with sodium ethoxide. Only a small quantity of 6-nitrofluoroanisole was available, but a single determination by the sodium carbonate method indicated the decomposition of 0·2%. From these results it is evident that the 4- and 6-nitro-derivatives do not decompose appreciably under the conditions used. On the other hand, 4-nitrofluoroanisole is decomposed at a measurable velocity at 85° by sodium methoxide of the dilution stated above, and, in this connexion, reference may be made to Holleman and Beekman's experiment on the alcoholysis of

m-nitrofluorobenzene (*Rec. trav. chim.*, 1904, **23**, 235). The mixed 3- and 5-nitroguaiacols were isolated from the above decompositions with sodium, but the quantity was too small for the estimation of their relative proportions by the steam distillation method employed by Ingold and Ingold (preceding paper). A small quantity of pure 5-nitroguaiacol was isolated by taking advantage of the sparing solubility of its potassium salt in 4*N*-aqueous potassium hydroxide.

4-*Nitro*-o-*fluoroanisole*.—The nitrofluoroanisoles recovered after decomposition of the 3- and 5-derivatives with sodium carbonate formed a mixture which was liquid at the ordinary temperature but, on cooling in an efficient freezing mixture, set to a paste of crystals. These were collected below −20°, and when freed from adhering oil, had m. p. 47—49°. By crystallisation from ligroin pale yellow prisms were obtained, m. p. 52—52·5°, which were identified by direct comparison and a mixed m. p. determination with a specimen synthesised as described below. The yield accounted for about 10% of the nitration product.

Synthesis of 4-*Nitro*-o-*fluoroanisole*.—4-Nitro-*o*-anisidine (25 g.) prepared from 2 : 4-dinitrochlorobenzene, *via* 2 : 4-dinitroanisole, was dissolved in 50 c.c. of boiling 20% hydrochloric acid, and the solution cooled with rapid stirring to ensure fine division of the solid. Diazotisation was effected in the usual way with 11 g. of sodium nitrite, and the mixture poured into a solution of 30 g. of potassium hydroxide and 13 g. of piperidine in 150 c.c. of water with the addition of sufficient ice to maintain the temperature at 0°. The oily precipitate soon solidified (yield, 35 g.), and crystallisation from ethyl alcohol gave buff needles, m. p. 95—96° (Found : C, 54·5; H, 6·0. $C_{12}H_{16}O_3N_4$ requires C, 54·2; H, 5·9%). This *diazopiperidide* (35 g.) was warmed on the steam-bath for 1 hour with 175 c.c. of concentrated hydrofluoric acid, the mixture being rapidly stirred at the commencement of the process. After the addition of ice the mixture was poured into 1·5 l. of 30% sodium hydroxide kept at 0°, and after complete neutralisation the mixture, which contained a brown precipitate of unknown constitution, was distilled in a current of steam. The nitrofluoroanisole crystallised in the receiver, but it was found convenient to extract it with ether. It melted at 45—49° in the crude condition and at 52—53° after crystallisation from ligroin (Found : C, 49·3; H, 3·5. $C_7H_6O_3NF$ requires C, 49·1; H, 3·5%). The yield was 1·3 g., that is, 7% of the theoretical.

On reduction by boiling for 15 minutes with stannous chloride and hydrochloric acid it was converted smoothly into *p*-anisidine, the elimination of fluorine being quantitative. The anisidine thus obtained melted at 56—57°, alone and when mixed with a genuine specimen (Found : C, 68·8; H, 7·5. Calc. : C, 68·9; H, 7·4%.

Calc. for C_7H_8ONF: C, 59·6; H, 5·7%). An application of this reaction is described below.

Synthesis of 6-*Nitro*-o-*fluoroanisole*.—The silver salt of 2 : 6-dinitrophenol was boiled with a benzene solution of methyl iodide, and the dinitroanisole so obtained was reduced by hydrogen sulphide in methyl-alcoholic ammonia solution to 6-nitro-*o*-anisidine (yield 35%). The *hydrochloride* of this base separated from hydrochloric acid in clusters of pale yellow needles, m. p. 198°.

The base was converted into its *diazopiperidide* by the method described in the preceding paragraph. The diazopiperidide, after draining on porous porcelain, but without further purification, was decomposed with hydrofluoric acid, and the 6-*nitro*-o-*fluoroanisole* isolated by distillation in steam. After redistillation it was obtained as a pale yellow oil, b. p. 110°/1 mm. (Found: C, 49·6; H, 3·7. $C_7H_8O_3NF$ requires C, 49·1; H, 3·5%).

On reduction by stannous chloride and hydrochloric acid *o*-anisidine was obtained unaccompanied by any fluoro-base.

Estimation of the Proportions of 4- *and* 6-*Nitro*-o-*fluoroanisoles obtained by Nitration*.—The mixture of 4- and 6-nitrofluoroanisoles obtained after decomposition of the 3- and 5-nitro-isomerides by sodium carbonate was reduced with stannous chloride as described above. The yield of distilled bases was 90% of the theoretical, and analysis showed that the whole of the fluorine had been eliminated (Found: C, 69·1; H, 7·2%).

A weighed portion of these mixed bases was treated with hydrochloric acid; *o*-anisidine hydrochloride (m. p. 225°, alone and mixed with an authentic specimen; a mixture with *p*-anisidine hydrochloride, m. p. 215°, melted at 170—180°) was thus obtained. The yield corresponded with 48% of 6-nitrofluoroanisole in the original mixture.

In order to estimate the relative proportions of *o*- and *p*-anisidine in the mixture of these bases, a series of artificial mixtures, in the proportions 20 : 80, 40 : 60, 60 : 40, and 80 : 20, was prepared in the form of 1% solutions in ethyl alcohol. Each of these was tested in turn against a 1% solution of the experimental mixture, equal volumes of the solutions under comparison being added to equal portions of a solution of ferric chloride in similar colorimeter tubes. By comparing the colours, it was found that the proportion of *p*-isomeride in the experimental mixture lay between 20% and 40%. The process was repeated with three more standards, containing 25%, 30%, and 35%, respectively, of *p*-compound. As these tests indicated that the proportion of *p*-isomeride lay between 30% and 35%, an additional standard, containing 32·5% of *p*-anisidine and 67·5% of *o*-anisidine, was made. This agreed as exactly as could be

ascertained with the experimental mixture, both as regards rate of development of the colour and its maximum intensity. The conditions being so adjusted that about 2—4 minutes were required for the colour to reach its maximum intensity, it was found that the rate of development of colour was more sensitive than maximum intensity to changes of composition and served as a better means of comparison. In the final experiments, therefore, all solutions were immersed in the same bath before mixing, and to avoid differences of temperature during the readings the two tubes were surrounded by a metal screen and symmetrically illuminated. The results are believed to be correct to 2%.

On acetylation of the experimental mixture of bases, a mixture of acetyl derivatives was obtained which set at 59°, and admixture with small amounts of either aceto-*o*-anisidide or aceto-*p*-anisidide raised this setting point, whence it appears that the proportion in which the two substances were present in the acetylation product corresponds approximately with the eutectic composition. The following approximate setting points of mixtures of aceto-*o*-anisidide and aceto-*p*-anisidide indicate that the eutectic contains about 31% of the *p*-compound and sets at 60°, and this supplies confirmation of the figure obtained colorimetrically :

Proportion of para- ...	17·3%	21·4%	24·4%	30·6%	35·0%	39·1%
Setting point	71°	67·5°	64°	60°	63·5°	67°

These values were determined by the cooling curve method.

We wish to thank the Chemical Society and the Royal Society for grants with the aid of which the expenses of this investigation have been met.

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CLXXI.—*A Method for Determining the Solubility of Sparingly Soluble Substances.*

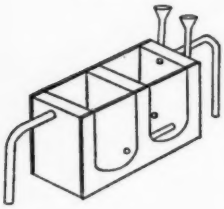
By STOTHERD MITCHELL.

THE methods available for determining the solubility of sparingly soluble substances are of limited application. Electrical measurements are restricted to electrolytes, and chemical analysis is useful for only a few substances. The optical method now described can, however, be employed more generally.

For this work, an interferometer of the type described by Jamin (*Ann. Chim. Phys.*, 1858, **52**, 171) was constructed. Mercury green

light ($\lambda = 5461$) was used throughout as the source of illumination. A special form of double cell was required in which liquids could be circulated through each compartment (Fig. 1). It was cut from a rectangular block of brass (2·5 cm. broad), and was fitted with inlet and outlet tubes of the same metal. The sides were made of the best quality optical glass cemented in position. Both compartments of the cell were first filled with water, and the compensator was adjusted so that the cross wires of the observing telescope coincided with one of the interference bands. When a dilute aqueous solution was gradually allowed to displace the water in one half of the cell, there was a movement of the bands. By means of a fine adjustment on the compensator the same band could be kept on the telescope cross wires.

FIG. 1.



Over the range considered, the compensator readings increased in proportion to the number of bands displaced, and therefore to the difference in refractive index between the contents of the two compartments of the cell (Table I).

TABLE I.

Bands.	0.	2.	4.	6.	8.	10.	12.	14.	16.	18.	20.
Compensator readings ...	10	13·6	17·0	20·5	24·0	27·7	31·5	35·0	39·0	43·0	46·5

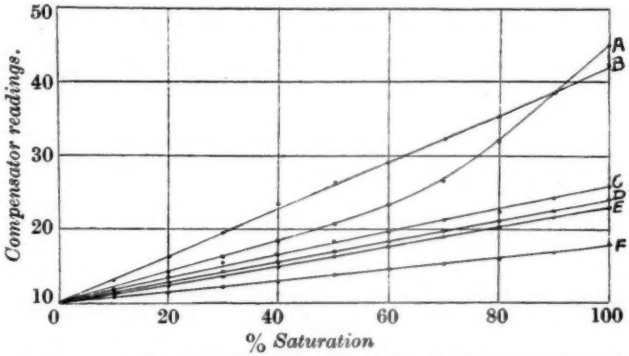
As a preliminary it was necessary to investigate the nature of the curves correlating compensator readings and concentration. To do this, a number of saturated solutions of substances slightly soluble in water were prepared at room temperature. A series of dilutions of each was made, and these together with a quantity of water were allowed to stand until all were at the same temperature. Both divisions of the cell were then filled with water, and the zero-reading was taken. Water was allowed to circulate through one compartment, and the most dilute solution through the other. When no further movement of the bands took place, the reading was noted. The next solution was then allowed to displace the more dilute, and so on till the saturated solution was reached. A number of results are shown in Table II and Fig. 2. All substances so far investigated give straight lines with the exception of benzene. In view of this exception, it will always be necessary to plot a graph of % *saturation* against *compensator readings* as a preliminary to a solubility determination by this method. When the graph is a straight line, only one weighing is necessary to calibrate the concentration scale, and if the reading for the saturated solution is

TABLE II.

Substance.	Compensator readings for % saturation. 0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	100.
Benzene	10·0	12·6	14·3	16·2	18·5	20·8	23·5	26·5	32·0	38·5	45·0
Camphor	10·0	12·8	16·3	19·8	23·6	26·7	29·0	32·2	35·6	38·7	43·2
sec.-Octyl alcohol	10·0	12·4	14·0	15·5	16·8	18·8	20·0	21·5	22·4	24·5	26·0
Borneol	10·0	11·5	12·8	14·1	15·3	16·7	18·3	19·4	20·8	22·3	24·0
Methyl salicylate	10·0	11·0	12·2	13·5	15·0	16·4	17·9	19·1	20·3	21·6	23·0
Naphthalene.....	10·0	11·0	11·5	12·0	12·6	13·7	14·3	14·8	15·5	16·8	18·1

determined the weight of the solute present in it can be found graphically by extrapolation. In practice, it is advisable to prepare one or more dilutions from the solution of known concentration so that there may be a gradual movement of the bands without

FIG. 2.



A. *Benzene.* B. *Camphor.* C. sec.-*Octyl alcohol.* D. *Borneol.* E. *Methyl salicylate.* F. *Naphthalene.*

blurring. Should the graph not be a straight line, a number of weighings would be necessary and the method would lose its merit of simplicity.

When a solubility is required at a temperature other than room temperature, a saturated solution is prepared at that temperature and separated off; then, if necessary, a known quantity of water is added so that the solute will remain completely in solution at the temperature of the room in which the readings are taken. The saturated solutions were prepared in stoppered bottles which were rotated in a thermostat with excess of solute for several hours at the required temperature. Table III shows a number of results.

As an indication of the accuracy with which these results could be reproduced, it may be mentioned that a duplicate determination with lead sulphate gave the same value as shown, *i.e.*, 0·032 at 15°,

TABLE III.

[In each case, Solution A_1 was made up as shown in column 2, and Solution A_2 was a two-fold dilution of A_1. These were used for the standardisation, by means of which the concentrations of B_1 (saturated) and B_2 (half-saturated) were deduced from their compensator readings.]

	G. of substance	Compensator readings.					Solubility (g. per
Substance.	in 1000 c.c. of water.	Soln. A_1.	Soln. A_2.	Soln. B_1.	Soln. B_2.	Temp.	1000 c.c. of water).
Naphthalene ...	0·0200	14·0	12·0	14·5		15°	0·022
					14·0	25	0·040
Lead sulphate	0·0250	11·4	10·7	11·8		15	0·032
Borneol	0·5000	18·3	14·3	21·4		15	0·693
					16·2	25	0·740
sec.-Octyl alcohol	1·0407	19·0	14·5	23·5		15	1·508
				21·5		25	1·280

and two additional experiments with borneol gave the following results: 0·697, 0·697 at 15°; 0·740, 0·734 at 25°.

Water has been used as solvent in these experiments, but the method could be extended to other solvents if they are not too volatile.

The author desires to thank Miss Janet M. Henderson for assistance with the experimental work.

UNIVERSITY OF GLASGOW. [*Received, February 15th,* 1926.]

CLXXII.—*The Inhibition of the Glow of Phosphorus.*

By HARRY JULIUS EMELÉUS.

THE slow luminous oxidation of phosphorus is influenced by the addition of a gas or vapour in one of two ways. Gases such as hydrogen, nitrogen, and carbon dioxide effect a dilution, and the kinetics of the reaction continue to obey the law of mass action. In other cases, however, (*e.g.*, many organic vapours) a small concentration of the added substance stops the reaction and the accompanying phenomena of ionisation and formation of ozone. Phosphorus has, moreover, the remarkable property of oxidising much more slowly, and without luminescence, in pure oxygen when the partial pressure of this gas exceeds a limiting value determined by the temperature. The existence of such a pressure is readily demonstrated by gradually evacuating a vessel containing phosphorus and oxygen. At atmospheric pressure, the reaction is imperceptible, but when the "glow pressure" is reached the phosphorus surface lights up suddenly as the normal oxidation begins. Apparently in this case the oxidation is inhibited by oxygen itself.

Various suggestions have been made to account for these anomalies. One of the earliest was that the ozone formed during the reaction was an essential catalyst, and that it was destroyed by the poisons (Schönbein, *J. pr. Chem.*, 1845, **36**, 246). It is remarkable how often such a reaction is found to be possible. For example, turpentine, ethylene, and benzene can all act as inhibitors, and all react readily with ozone, yet in other cases any such action is very much feebler. Qualitative tests were made to examine the action of ozone on acetone, methyl ethyl ketone, hexane, chlorobenzene, and ethyl iodide. The first three gave definite evidence of a slow reaction, whilst the last two were more readily attacked. It is evidently wrong to assert that any of these substances is quite inert. If this were the true explanation of inhibition, however, the relative activity of different poisons would presumably be that of their reactivity towards ozone, and in some cases this is not so; *e.g.*, acetone is a stronger poison than benzene, but is less readily attacked by ozone.

The alternative suggestion that poisons form protective surface films on the solid phosphorus is unlikely, for Centnerszwer has shown that phosphorus exerts its normal vapour pressure in presence of inhibitors (*Z. physikal. Chem.*, 1913, **85**, 99).

The view now generally held is that the propagation of the glow is a process analogous to the passage of a flame through a combustible gas mixture, and that poisons prevent this from occurring. Lord Rayleigh has, in fact, shown that this is probably correct in the particular case of inhibition by excess of oxygen (*Proc. Roy. Soc.*, 1923, *A*, **104**, 322). Extending the earlier experiments of Bloch (*Compt. rend.*, 1908, **147**, 842), he measured the blast of gas necessary to blow the glow from a given phosphorus surface in various oxygen–nitrogen mixtures, and found that it became less as the percentage of oxygen was increased. Assuming that the blast required to maintain the glow in a stationary position downstream is a measure of the virtual rate of propagation upstream, it follows that successive increases in the oxygen concentration decrease the rate of propagation.

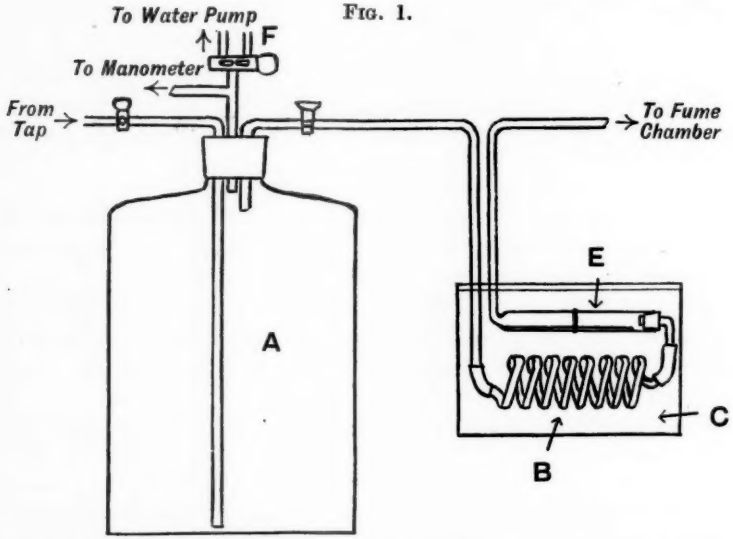
The position of oxygen is unique, since it both supports and inhibits combustion, and it cannot be assumed *a priori* that the more active poisons act in the same way. In the experiments to be described, this point has been studied by applying Lord Rayleigh's method of investigation to the propagation of the glow in presence of the strong inhibitors ethylene, benzene, chloroform, and aniline, and results similar to those for oxygen have been obtained.

The Propagation of the Glow of Phosphorus in the Presence of Inhibiting Substances.

The phosphorus used throughout was purified by an acid dichromate solution, as described by Downey (J., 1924, **125**, 347). Oxygen was obtained from a cylinder.

The apparatus consisted of a large bottle, A (Fig. 1), into which water was run from the tap. The gas stream so produced was passed through the metal coil, B, where it attained the temperature of the bath, C, and then over a flat phosphorus surface cast in the cylindrical tube, E (14 cm. long, 1 cm. internal diameter). Round

FIG. 1.



E, about half-way along, a narrow black band was fixed, and in all the experiments the gas stream was adjusted so as to blow the glow from the phosphorus surface up to this mark. From a direct measurement of the rate at which water was flowing into A, the velocity of the blast through E could be calculated.

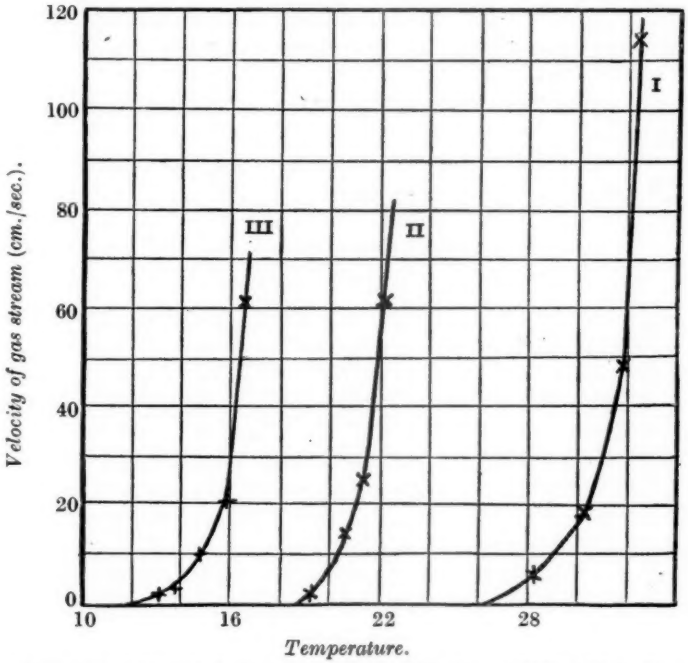
Dependence of the Blast upon the Percentage of Ethylene added to the Air.—To obtain the low concentrations of ethylene (less than 0·5%), a mixture of ethylene and air in known proportions was prepared in a gas holder connected to F (Fig. 1). A was then evacuated, and the ethylene–air mixture and air were admitted in the desired proportions as indicated by the mercury manometer. The solubility of the ethylene in the water during the short time of contact was neglected as being within the limits of experimental error. The same phosphorus surface was used throughout. Measurements of the

gas stream needed to blow the glow to the mark were made for different ethylene concentrations at a temperature of 20°. In this way, a series of relative values was obtained, showing the influence of the admixed gas on the propagation of the glow :

Velocity of gas stream (cm./sec.)	140	31	24	17	8	1	1
% Ethylene (by volume)	0·16	0·26	0·28	0·36	0·38	0·43	0·46

With less than 0·15% of ethylene the greatest gas stream obtainable was insufficient to blow the glow off the phosphorus surface. As the

FIG. 2.



Air saturated (I) *with benzene ;* (II) *with chloroform ;* (III) *with aniline.*

ethylene concentration was increased it became easier to blow the glow away, and complete inhibition occurred at a concentration of 0·45%.

Dependence of the Blast upon the Temperature, in the Presence of a Constant Concentration of Inhibiting Substance.—Three typical poisons, benzene, chloroform, and aniline, were introduced in large excess into A (Fig. 1) in successive series of experiments, and the air was allowed to become saturated with the vapour at room temperature (16°). The blast of saturated gas which just sufficed to clear the phosphorus surface of luminosity was then determined as

already described for various temperatures of the bath, C. The results are reproduced in Fig. 2. In each case the glow was inhibited below a certain temperature, and above this it became increasingly difficult to blow it away.

If Lord Rayleigh's assumption be adopted, it follows from these results that the typical poisons studied act by reducing the rate of propagation of the glow in the gas mixture. Complete inhibition of the luminous oxidation marks the limit of this effect with increasing concentration of inhibitor. It is very probable, therefore, that oxygen acts in the same way as the more active poisons. A discussion of the possible mechanism of inhibition is given later. These considerations might seem inapplicable to the conditions under which the glow of phosphorus is generally seen, *viz.*, as a surface luminosity. The establishment of this intense surface oxidation is, however, often preceded by the passage of a luminous pulse through the gas mixture, resulting in the production of ozone, which tends to localise the reaction.

The Influence of Temperature on the Action of Inhibiting Substances.

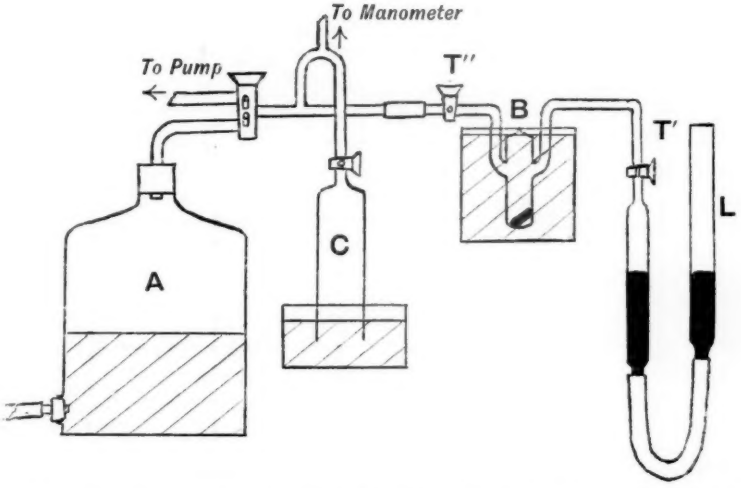
The effect of "poisons" depends both on the pressure and on the temperature. The influence of pressure was investigated by Centnerszwer (*Z. physikal. Chem.*, 1898, **26**, 1). Phosphorus was introduced into a mixture of oxygen with the inhibiting vapour, and the pressure was reduced until the glow appeared. In every case the limit was lower the greater the concentration of the inhibitor. The present experiments represent an attempt to make a similar systematic study of the influence of temperature. Ethylene has been used, since it is not only a strong poison, but is inert towards phosphorus. Probably it is typical, however, for experiments made with carbon disulphide and ethyl iodide gave similar although less consistent results.

The apparatus used is shown in Fig. 3. Ethylene was prepared from phosphoric acid and absolute alcohol, washed by water and sulphuric acid, and collected over water in A. Between 2—5 g. of purified phosphorus were sealed up in the tube B of 30 c.c. capacity, which was immersed in a freezing mixture and evacuated, with the tap T′ closed and the space below it filled with mercury. B was then put in melting ice, and ethylene was admitted from A. After allowing time for diffusion, moist air or oxygen was passed in from C until the total pressure was that of the atmosphere. The tap T″ was then closed and T′ opened. B was heated gradually on a water-bath over a resistance mat, and the temperature at which the glow appeared was recorded. During heating, the pressure in the apparatus was kept constant by adjusting the levelling tube,

L. Between successive experiments with different ethylene–air mixtures, the space below T′ was filled with mercury, T′ was closed, B was cooled, and the apparatus was alternately evacuated and filled with air a number of times. Some consecutive pairs of observations were made with the same phosphorus, in which a definite partial pressure of ethylene was established first in air and then in oxygen. Such readings were strictly comparable, and differed by less than 3°. The oxygen–ethylene mixtures frequently detonated shortly after the phosphorus had begun to glow.

Experiments were made at constant volume by raising the tube L (Fig. 3). The resulting increase in pressure amounted at the

FIG. 3.



highest temperature employed to approximately half an atmosphere, and a corresponding increase in the glow temperature of 5—10° was recorded. The results are shown graphically in Fig. 4.

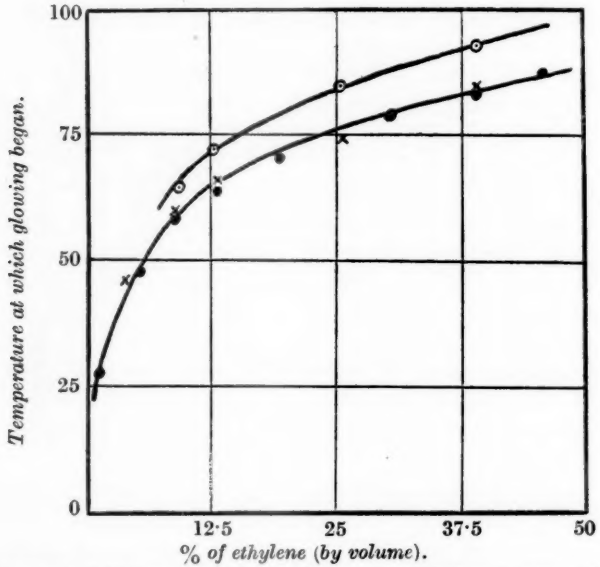
The main source of error in these experiments was in the observation of the glow. Even with thoroughly rested eyes it was difficult to determine in some cases whether a glow was occurring or not, especially with the high ethylene concentrations.

Two points of special interest are brought out by these results. The temperature at which the glow first occurred appeared to be determined by the concentration of the ethylene, irrespective of whether it was mixed with air or oxygen; also the luminous oxidation was inhibited at temperatures well above the normal ignition-point of phosphorus, which is about 60°.

Although these experiments leave little doubt as to the absence

of luminous oxidation below a definite temperature, a number of tests were made to determine if any non-luminous oxidation occurred. Purified phosphorus (1—2 g.) was sealed in tubes of 40 c.c. capacity (1·5 cm. diameter), having a quill tube fused to one end and drawn down to a capillary about 20 cm. from the wider tube. The whole tube up to the capillary was cooled in a freezing mixture and evacuated; the freezing mixture was replaced by melting ice, moist ethylene and air were admitted in the desired proportions, as indicated by the pressure, and the tube was sealed at the capillary. Two series of bulbs, containing 8% and 26%, respectively, of

FIG. 4.



⊙ *Ethylene-air mixtures at constant volume.* × *Ethylene-oxygen mixtures at constant pressure.* ● *Ethylene-air mixtures at constant pressure.*

ethylene were heated in the dark in a thermostat at 48° for 2 months, when they were opened by breaking the capillary under mercury, the bulb being inverted and cooled in ice. Any oxidation would be indicated by a rise of mercury in the stem, correction being made for change in barometric height. The bulbs containing 8% of ethylene exhibited a decrease in pressure of 2—12 cm. of mercury, whilst for those with 26% the decrease varied between 2—6 cm. Control tubes containing no phosphorus were unaltered. Further experiments are being made to verify that this slow rate of oxidation is maintained.

These results show that absorption of oxygen occurs when the

luminous oxidation is inhibited, which is analogous to Lord Rayleigh's observation of a slow non-luminous oxidation in moist oxygen at atmospheric pressure (*Proc. Roy. Soc.*, 1924, *A*, **106**, 1).

Discussion.

Any account of the mechanism of inhibition must explain why either an increase in temperature or a decrease in pressure tends to produce the glow. The former involves at least two factors, since both the vapour pressure of the phosphorus and the potential rate of reaction increase. The experiments described have shown that inhibition can extend to 90°, which is much above the normal ignition temperature of phosphorus. Moreover, the "glow temperature" does not depend on whether air or oxygen is used as a diluent for the ethylene. When the glow is prevented, the tendency for the reaction to occur is demonstrated by the slow non-luminous oxidation which was observed at 48°. At some stage, depending on the ethylene concentration, the impediment is overcome and a wave of luminosity passes through the mixture, the subsequent oxidation being accelerated by the formation of ozone. Again, on slowly decreasing the pressure in a mixture of ethylene and oxygen, the partial pressure of the phosphorus will remain constant in the presence of the solid. In effect, therefore, the proportion of combustible vapour in the mixture is being increased, which in itself would be expected to favour flame propagation.

Several analogous cases have been recorded. White found that the vapours of benzene, acetaldehyde, acetone, and ether had "a powerful inhibitory effect on the propagation of flame in carbon disulphide–air mixtures" (J., 1922, **121**, 2561). The addition of 0·025% of ether, for example, necessitated the use of 25% more carbon disulphide if the mixture was to propagate flame. In Dixon's experiments on the phosphorescent flame of carbon disulphide, a very much higher temperature was required to produce ignition when a small amount of ethylene was added (*Rec. trav. chim.*, 1925, **44**, 305). Further examples are furnished by the many organic sulphur compounds studied by Delépine (*Bull. Soc. chim.*, 1922, **31**, 762). These contain the group C=S, or P=S, and undergo a luminous oxidation at room temperatures, which is inhibited by ether, acetone, and pyridine. Here also a decrease of pressure or an increase of temperature will restart the luminescent reaction after it has been arrested.

The experiments described have shown that the addition to air of typical inhibitors renders it easier to blow the glow from a phosphorus surface, and that increase in temperature diminishes this action. An analogy is thus established between the action of

excess of oxygen and that of stronger poisons, in that both prevent the propagation of the glow in the gas. A tentative explanation of the mechanism was put forward by Lord Rayleigh, who suggested that in the propagation of the glow the products of the reaction in one layer acted as catalysts in the next. These catalytic particles are supposed to be rendered inactive by the adsorption of the inhibiting molecules, when the reaction stops. A similar view has been adopted by Dixon to explain the inhibition of the phosphorescent flame of carbon disulphide.

The author wishes to thank Professor H. B. Baker, F.R.S., for his kind interest and advice throughout this research. He is indebted to the Department of Scientific and Industrial Research for a maintenance grant, and to the Trustees of the Dixon Fund for a grant for the purchase of apparatus.

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LONDON, S.W. 7. [*Received, February 12th*, 1926.]

CLXXIII.—*An Improved Hydrogen Sulphide Generator.*

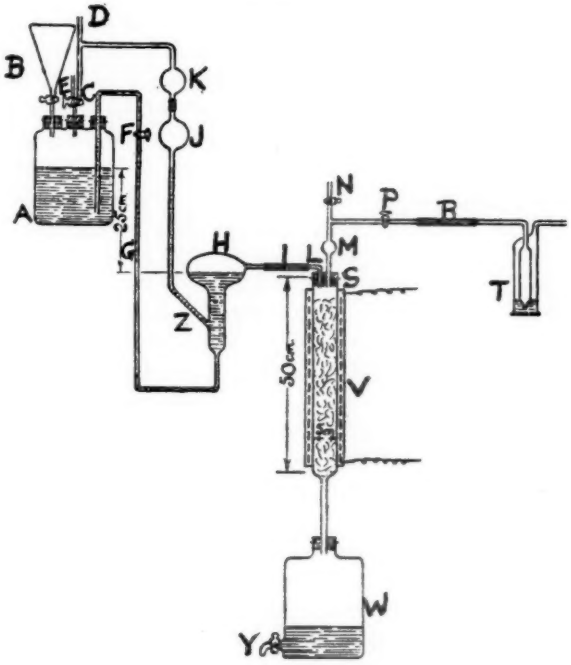
By HENRY GEORGE DENHAM and JOHN PACKER.

AN automatic hydrogen sulphide generator for laboratory installation has been described by Steele and Denham (J., 1920, **117**, 527). Since then the present authors have redesigned certain portions of the apparatus and the modified generator has given such highly satisfactory results during constant use for the last two years that a description of it is considered justified. A laboratory fitted with one of these generators would have a potential and practically unlimited supply of hydrogen sulphide always at hand at the negligible cost of the electric current needed to keep the generator heated.

The following is a description of the apparatus. A is the acid-holder of about 6 litres capacity; B a tap-funnel for use in filling A; C a two-way tap so that A can be connected either to the tube D which leads to an outside flue, or to E; F is a large-bore tap situated at a higher level than the acid in A; H is a reservoir of 600—700 c.c. capacity for retaining hydrogen sulphide generated, but not withdrawn from the apparatus; J is a bulb of about 150 c.c. capacity, situated a few cm. above the highest level of acid in A; K is a 100 c.c. bulb; L is a piece of capillary tubing of 2 mm. bore and of about 8 cm. total length, used to prevent a too rapid flow of acid into V, connected to the reservoir H by a piece of pressure

tubing I (wired on); M is a small 10 c.c. bulb, N and P are taps, R is thick-walled rubber tubing, inserted for flexibility so that the rubber stopper S can be easily removed; T is a wash-bottle containing water, through which the hydrogen sulphide is supplied to the distributing taps and mains; V is a tube of fused silica, the upper portion of which is about 50 cm. long and 5 cm. internal diameter whilst the lower part is of 2 cm. internal diameter, fitted by a tight rubber stopper into the reservoir, W, of 6 litres capacity, which receives the spent acid; Y is a tap through which the spent

FIG. 1.



acid is withdrawn, connected to a waste drain. The tube V is heated electrically to a temperature of approximately 80°. The winding (total resistance 100 ohms) is made over a thin piece of asbestos paper with nichrome wire of 1 ohm per foot resistance, and is well covered with many thicknesses of asbestos paper. In the authors' generator, this winding is connected through an ammeter and adjustable resistance to a storage battery in such a way that it can be connected either with the full battery of 110 volts or a portion of it giving 60 volts. A current of just over 1 amp. is sufficient to heat the tube V up to the working tem-

perature in from 10 to 15 minutes, whilst a current of 0·6 amp. will maintain this temperature.

Mode of Operation.—The tube V is packed with lumps of iron sulphide. The acid-holder is filled by means of the funnel B with commercial hydrochloric acid diluted with an equal volume of water, and the funnel tap turned off. The taps F and N are turned on and the tap C is turned so as to connect the acid-holder to E, through which air is blown until the siphon, G, fills. Tap N is then turned off and tap E turned so as to connect the acid-holder with the tube D. The reservoir H fills to the side-tube level with acid which then runs over into V and, provided the tube V has been sufficiently heated, hydrogen sulphide is generated as soon as a few drops run over, and drives the acid back into H, where the gas is stored until drawn off through the tap P and wash-bottle T. The acid is completely neutralised long before it has percolated through the heated column of sulphide. The side-tube Z and bulbs J and K are provided as an escape for hydrogen sulphide should an excessive amount be generated owing to some abnormal cause. This prevents hydrogen sulphide from getting into the siphon and putting the generator out of action. When the generator is not in operation and the tube V not heated, tap F is kept turned off.

General Remarks.—The capacity of this generator is practically the same as that of the one formerly described, whilst almost theoretical yields of hydrogen sulphide are always available at a steady and convenient pressure. It has the following advantages over the older form: (1) It is completely automatic in operation. From this point of view electrical heating is a great advantage over steam heating, whilst the use of silica instead of glass for the tube V overcomes the trouble formerly experienced of cracking, due to alternate heating and cooling. (2) There is no leakage of acid, as it never comes into contact with the rubber stoppers or connexions (except at I during a portion of the cycle of operations). (3) Provided the tube D is carried to a suitable flue, there is no smell of hydrogen sulphide.

The hydrogen sulphide is distributed throughout this building in composition (lead) gas-pipes of $\frac{1}{4}$ in. internal diameter without any serious loss of pressure. After 3 years the attack on these pipes appears scarcely to have penetrated beyond the inner surface, although in the experience of one of the authors in the sub-tropical climate of Brisbane these pipes were seriously attacked, but this could probably be overcome by the use of drawn copper tube.

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CHRISTCHURCH. [*Received, March 22nd*, 1926.]

CLXXIV.—*The Doubtful Existence of Aurous Oxide.*

By William Branch Pollard.

It has been found that mercurous nitrate and chloroauric acid react to form gold and a basic auric compound (this vol., p. 529), and not "aurous oxide" as claimed by Figuier (*Ann. Chim. Phys.*, 1844, **11**, 339) and Krüss (*Annalen*, 1887, **237**, 276). In consequence of this, "aurous oxide," prepared in other ways, has been examined to see if it might not consist of colloidal gold and auric hydroxide. Analogous substances are known, such as Purple of Cassius, in which metallic hydroxides function as protective colloids.

From the equation $3Au_2O = 4Au + Au_2O_3$ it is clear that the determination of gold and oxygen cannot show whether the substance is aurous oxide or a mixture of gold and auric oxide in these proportions. This possibility was overlooked by Krüss, whose analyses are therefore inconclusive. Krüss's claim is, moreover, unsupported by any chemical evidence showing that aurous compounds can be formed from "aurous oxide."

Experimental.

In attempts to prepare "aurous oxide" from potassium bromoaurate by Krüss's method, if an excess of potassium bromide was present, only metallic gold resulted. "Aurous oxide" was decomposed when heated with solutions of potassium bromide, but was much less decomposed by solutions of sodium chloride. As potassium bromide is a by-product in the formation of "aurous oxide," it is surprising that Krüss was able to obtain his substance in the proportions required by theory.

By the following slight modification it was found possible to work at room temperature. Gold (1·0 g.) was converted into chloroauric acid, made up to 1 litre with saturated sodium chloride solution, and reduced to the aurous state with sulphurous acid. The solution, now colourless, was made slightly alkaline with caustic soda. Very little precipitation occurred at first, but a black, colloidal substance separated on standing. Heat caused the precipitation to occur rapidly. The formation of the substance is therefore quite unlike that of metallic hydroxides, but is highly suggestive of the decomposition of aurous compounds.

The substance formed a dark blue, colloidal suspension when washed with cold water, but could generally be washed with hot water. With hydrochloric or hydrobromic acid it instantly formed metallic gold and chloroauric or bromoauric acid; the reaction did not suggest the slow decomposition which takes place in aurous

compounds. The addition of alkali metal chlorides or bromides to the corresponding acids failed to produce aurous compounds (Lenher, *J. Amer. Chem. Soc.*, 1913, **35**, 547). Hydriodic acid gave gold, aurous iodide, and iodine; with excess of the reagent, aurous iodide passed into solution. This reaction resembles that of hydriodic acid and auric oxide:

$$Au_2O_3 + 6HI = 2AuI + 3H_2O + 2I_2.$$

Although these reactions were known to earlier workers, no reason has been given to explain why iodine should be liberated by "aurous oxide."

With a solution of sodium sulphite, the substance formed sodium aurosulphite and left a residue of gold which had the same black colour as the original substance. With sodium thiosulphate, it formed sodium aurothiosulphate and left a residue of black gold. In both these cases an aurous compound is formed, but only a third of the gold takes part in the reaction and this has to undergo reduction.

When the substance was heated with strong nitric acid a residue of gold was left and a yellow solution was formed which, on dilution, hydrolysed with the separation of auric hydroxide.

When heated with potassium bromoaurate solution, gold dissolved and was deposited, on cooling, in shining crystals according to the equation $AuBr_3 + 2Au \rightleftharpoons 3AuBr$.

When the substance was heated with potassium bromide solution, a residue of brown gold was left and gold passed into the solution, which then became strongly alkaline. Potassium iodide behaved in the same way, but was more energetic in its action. Sodium chloride solutions were much less reactive. Although no previous reference could be found, auric hydroxide was shown to behave in exactly the same way, dissolving even in strong sodium chloride solution which thus became alkaline. The reaction, however, was most marked in the case of potassium iodide.

The substance was scarcely attacked by dilute caustic soda, but with strong solutions sodium aurate and metallic gold were formed. Auric oxide was slowly attacked by weak but rapidly attacked by strong solutions of caustic soda. This explains why Krüss found it necessary to employ "very weak potash" in the formation of his "aurous oxide," strong alkali preventing its formation just as strong hydrochloric acid prevents the formation of Purple of Cassius.

Although numerous reactions have been tried, in no case has any definite aurous reaction been discovered, the substance always behaving as a mixture of gold and auric hydroxide. As the sub-

stance is highly colloidal, any attempts at a mechanical separation into gold and auric hydroxide would present very great difficulty. Experiments were made, however, to see whether auric hydroxide could act as a protective colloid in the manner suggested.

Auric hydroxide prepared by the magnesia process was washed in a centrifuge with cold water until it began to pass into colloidal suspension just as Krüss's "aurous oxide" does. Portions were then taken, made alkaline with caustic soda, and partly reduced to gold by dilute solutions of various reducing agents. Little reaction occurred at first, but when the solutions were warmed or made more alkaline reduction set in. Further additions of reducing agent were made until the action was judged to have proceeded far enough; the precipitates were then separated in a centrifuge and washed. Black precipitates which appeared to be identical with Krüss's "aurous oxide" were thus obtained, with hydrazine, phenylhydrazine and formaldehyde as reducing agents. With sodium peroxide as reducing agent, a brown precipitate was obtained which transmitted red light but was otherwise identical with "aurous oxide."

No evidence has therefore been obtained to show that aurous oxide exists; its chemical and physical properties are those of a mixture of gold and auric hydroxide.

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CLXXV.—*Studies with the Microbalance. Part IV. The Photochemical Decomposition of Silver Iodide.*

By ERNST JOHANNES HARTUNG.

EXPERIMENTAL investigation of the action of light on silver iodide has hitherto furnished no definite result; when insolated in air, the substance slowly becomes greenish-grey, but the actual amount of chemical change appears to be very small and no free halogen has been detected. Koch and Schrader (*Z. Physik*, 1921, **6**, 127) illuminated very minute particles of silver iodide, suspended between the charged plates of a condenser, but could find no changes in weight greater than 1—2%. Koch and Vogler (*Ann. Physik*, 1925, **77**, 495) examined the space lattice of silver iodide by *X*-ray methods; after exposure to sunlight for 4 months, no free silver could be detected, although this was readily found on illumination of silver chloride and bromide for much shorter periods. Various other methods have given negative or indefinite results, although the consensus of opinion appears to be that the change is different

in nature from the decomposition of the bromide and chloride. Some years ago, the author showed (J., 1922, **121**, 689) that very thin films of silver iodide deposited on vitreous silica lost weight appreciably when exposed in air to sunlight; the losses were very much smaller than those found for the bromide and chloride, but there was no doubt as to their reality. A thorough study of the question has now been made by means of the Steele-Grant microbalance, on the general lines used successfully in the cases of the bromide and chloride (J., 1924, **125**, 2198; 1925, **127**, 2691) and it has been found that the photochemical decomposition of silver iodide is analogous to that of the other halides of silver; iodine is liberated and, under suitable conditions, the action may be made almost complete. The microbalance employed carried a load of 105 mg. and weighed with precision to 10^{-4} mg.; it had been thoroughly tested for 2 years and was used in very favourable circumstances. The general plan of the work was to iodinate thin films of chemically deposited silver until pure iodide had been formed. The films were then exposed to sunlight for various periods in oxygen, hydrogen, or nitrogen in the presence of a suitable iodine absorbent and subsequently reweighed. The insolated material was then treated in various ways in attempts to discover its nature. A series of experiments on the rate of iodination of silver, and of previously insolated silver iodide, was also made.

Preparation of Films of Pure Silver Iodide.—Light vitreous silica sheets were silvered in the well-known tartrate solution and ignited at 400° in a small electric furnace to drive off all occluded matter. After weighing, these films were hung over carefully purified iodine at room temperature; pearly-yellow iridescent silver iodide was rapidly formed and the films were then reweighed. Comparison of the weights with those calculated from the weight of silver taken showed an average discrepancy of 1 part in 1300 parts; the average weight was 0·34 mg. and the thickness about 0·0002 mm. Precipitated silver iodide is known to adsorb iodine readily, but no evidence of adsorption, or of the formation of polyiodides, was obtained in these experiments.

Photochemical Decomposition of Silver Iodide.—The glass apparatus in which the films were sealed, prior to insolation, was similar to that employed for silver bromide and has already been described (*loc. cit.*). Great care was necessary to prevent damage to the films by flame gases during sealing operations, but repeated tests showed that a good counter-current of purified air gave adequate protection. Before exhaustion, the vessel was filled with oxygen, hydrogen, or nitrogen, which had been specially purified and filtered. Experiments showed that at atmospheric pressure decomposition

of the silver iodide was very slow, even after prolonged exposure to strong sunlight, but was hastened by diminution of pressure. The apparatus was therefore exhausted either to 10 mm. pressure or as completely as possible. As heating of the glass walls was inadmissible owing to the sensitive nature of the films, adsorbed gas must have been released slowly during insolation; this is denoted by " res." (*i.e.*, " residual ") in Table I, to indicate that the pressure in the apparatus was less than 0·001 mm. at the time of sealing off from the pump. As absorbent for the liberated iodine, a roll of clean copper gauze was employed at first; this metal is particularly efficient in removing chlorine and bromine from a gas phase, but it was not successful with iodine. Inspection of the gauze after prolonged irradiation of the iodide film showed only slight evidence of tarnish, and at the same time the decomposition of the silver iodide had been very slow. Thus, after more than 6 months' exposure on the roof of the laboratory in an exhausted vessel containing copper gauze, a film of silver iodide weighing about 0·4 mg. had lost only 16·6% of its total iodine. This tardiness of decomposition indicated that the partial pressure of iodine vapour above strongly illuminated silver iodide is very small, for copper tarnishes readily above solid iodine at room temperature (partial pressure of vapour 0·2 mm.). It was subsequently found that silver absorbs iodine vapour with extreme readiness, even when the partial pressure of the halogen is very small, and consequently the lower portion and side-tube of the apparatus were silvered internally before introduction of the photosensitive film. During insolation, this silver deposit was shielded from radiation by opaque wrappings and a marked increase in the rate of decomposition of the halide was observed at once. In all subsequent experiments, therefore, silvering was adopted in order to render the absorption of iodine as complete as possible. The amount of radiant energy absorbed during insolation could not be measured, owing to the progressive change in the colour, opacity, and reflecting power of the films, but a fair indication is given in each case by the length of exposure in days. After a definite period of insolation, during which the film became deep slate-grey, the apparatus was opened under exhaust and purified nitrogen gradually admitted. The film was then removed and weighed; subsequent treatment consisted usually of re-iodination, but attempts were also made to analyse the product of insolation. Table I summarises the results of the experiments, weights being given in mg., and the columns headed F_1 and F_2 denoting the weights of the films after exposure and after re-iodination, respectively. It is evident that decomposition of the silver iodide proceeded very extensively, but only when the apparatus was exhausted;

TABLE I.

Expt.	Ignited Ag.	AgI. Found.	AgI. Calc.	F_1.	F_2.	% I lost.	Days.	Gas in apparatus.
1	0·1137	0·2475	0·2476	0·1250	0·2564	91·6	84	H_2 res.
2	0·1814	0·3954	0·3948	0·2102	0·3966	86·5	42	,, ,,
3	0·1120	0·2439	0·2438	0·1300	0·2452	86·3	52	N_2 ,,
4	0·1175	0·2558	0·2557	0·1335	0·2571	88·4	44	,, ,,
5	0·0701	0·1521	0·1526	0·0795	0·1552	88·5	36	,, ,,
6	0·2622	0·5705	0·5707	0·3355	0·5721	76·2	83	Air ,,
7	0·1095	0·2386	0·2383	0·1172	0·2402	94·0	89	O_2 ,,
8	0·1884	0·4101	0·4100	0·2548	0·4116	70·0	81	,, ,,
9	0·1884	0·4095	0·4100	0·4040	0·4153	2·5	86	O_2 10 mm.
10	0·1561	0·3396	0·3398	0·3341	0·3439	3·0	80	,, ,,
11	0·1797	0·3907	0·3911	0·3686	0·3905	10·5	90	N_2 ,,
12	0·1775	0·3863	0·3863	0·3775	0·3869	4·3	40	,, ,,

at 10 mm. pressure, the change was hindered in a remarkable manner. The nature of the residual gas in the apparatus seems to exert little influence and, in particular, the claim that oxygen is necessary is seen to be unfounded. Moreover, the extent of decomposition depends less on the period of exposure than on the thickness of the film, this being approximately proportional to the weight in each case. When all the factors are favourable, as in Expt. 7, decomposition is nearly complete. Certain minor irregularities in the results find a ready explanation in small variations in shape of the apparatus, which affect the ease of diffusion of the liberated iodine to the absorbing silver surface. There can be no doubt, however, that the products of insolation of silver iodide are silver and iodine, and the reason why extensive change is found only in very thin films is because of the opacity of the liberated silver and its very powerful attraction for iodine vapour. There is no evidence of the formation of any sub-iodide.

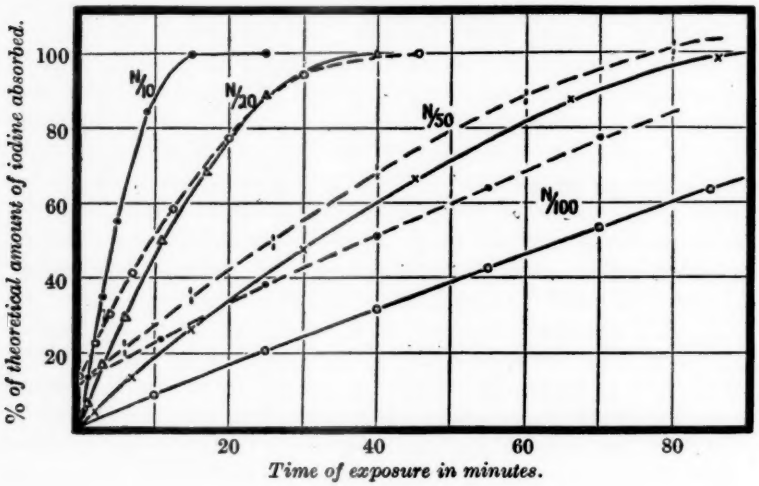
On re-iodinating the product of insolation, rapid restoration of the former yellow colour of the film took place and the weight was then usually rather greater than that of the original silver iodide. This behaviour was found with the chloride and bromide also and is believed to be due to slight oxidation of the insolated film during manipulation; the discrepancies are usually slight and, except for Expt. 1, are largest when oxygen in appreciable amount has been present in the exposing vessel (Expts. 9 and 10). Many attempts were made to analyse the product of insolation by methods which were devised for the filtration of very small amounts of material (this vol., p. 840), but no procedure for the accurate estimation of silver, or of silver iodide, in less than 0·5 mg. of a mixture of the two could be found. It was hoped to effect separation by suitable reagents, but solvents for silver (*e.g.*, nitric acid) removed the metal imperfectly from the iodide, whilst solvents for silver iodide (*e.g.*, silver nitrate, thiosulphates, cyanides) all attacked thin films

of silver rapidly in the presence of oxygen. Solution of both silver and silver iodide was easily effected by ammonium cyanide, which was then treated with acetic or hydrochloric acid; this precipitated all the iodide, and the remainder of the silver as either cyanide or chloride, but in each case the ammonium salt left in solution increased the solubility of the silver salts so markedly that no accurate results could be obtained. Also, estimation by simple evaporation of the ammonium cyanide solution to dryness was rendered useless by the formation of ammonium formate. Another attempted method consisted in evaporating the product of insolation with hydrochloric acid; the iodide was not affected by this treatment, but conversion of the silver presumably present into the chloride was so slow and imperfect that success was impossible. Finally, the attempts at analysis had to be abandoned, after showing that treatment of the product of insolation with silver iodide solvents left a residue of practically pure silver.

Rate of Iodination of Silver Films.—Further evidence as to the nature of the product of insolation of silver iodide was obtained by comparing its rates of re-iodination with those of pure silver. The apparatus and method have been described previously for the case of silver bromide (J., 1924, **125**, 2204); the experiments were carried out in a thermostat at 25° (regulated to 0·1°) and at first solid iodine was placed in the iodinator, giving a partial pressure in the vapour phase of 0·3 mm. However, silver films were attacked so rapidly that conversion into iodide was complete in less than 2 minutes and accurate measurements were impossible. Solutions of iodine from $N/10$ to $N/100$ were therefore made in N-aqueous potassium iodide, and the partial pressures of the halogen above these solutions (not measured) were sufficiently small to give convenient rates of iodination. The results obtained are shown in Fig. 1, in which the iodine absorbed, as percentage of that necessary to form pure silver iodide, is plotted against the total time of iodination in minutes. The continuous curves indicate iodination of pure silver, and the broken curves iodination of the product of insolation of silver iodide, which contained an average of 14% of the total original iodine at the start. In each case, the total area of the film was 146 sq. mm. and the thickness about 0·00015 mm., so that the curves are fairly comparable. The rapid increase in the speed of addition of the halogen as the solution increases in concentration is shown, as well as the striking similarity in speed between silver and insolated silver iodide for the same concentration of iodine which is evident from the approximate parallelism of each pair of curves. This is strong presumptive evidence that one of the products of insolation is silver itself, although, of course, differ-

ences in the physical state of the liberated metal may be expected to alter the rates of iodination very considerably, and indeed do so in the cases of the chloride and bromide. The peculiar phenomenon of an optimum halogen concentration which was discovered in the case of chlorine (J., 1925, **127**, 2696) has no parallel with iodine, where the rate of addition of the halogen steadily increases as the concentration in the gas phase rises. No evidence of the formation of sub-iodides or poly-iodides is indicated.

FIG. 1.



Summary.

1. The photochemical decomposition of silver iodide has been studied by means of the microbalance.

2. The maximum percentage loss of total iodine in thin films of silver iodide when suitably insolated was: in hydrogen 91·6%, in nitrogen 88·5%, and in oxygen 94·0%.

3. Evidence is adduced to show that the photochemical decomposition products are silver and iodine, that oxygen is not necessary for the change, and that extensive action is found only with extremely thin films at low gas-pressure in the presence of silver as iodine absorbent.

4. The rates of iodination of silver and of previously insolated silver iodide have been studied; close agreement exists between them for similar concentrations of iodine vapour.

5. No evidence of the formation of silver sub- or poly-iodides has been found.

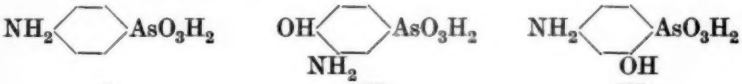
UNIVERSITY OF MELBOURNE. [*Received, April 7th*, 1926.]

CLXXVI.—*Trypanocidal Action and Chemical Constitution. Part V. Arylsulphonamides of some Phenylarsinic Acids.*

By LESLIE FRANK HEWITT, HAROLD KING, and WILLIAM OWEN MURCH.

PARTS I to IV in this series were almost solely devoted to the preparation, properties, and trypanocidal activity of arylamides of phenylarsinic acids, the common feature of the compounds described being the amide link, –CO·NH–. The present communication is designed to fill the gap in our knowledge of some of the corresponding sulphonamides, with the common link, $-SO_2\cdot NH-$, a group of which only two representatives, both non-amphoteric, have hitherto been described.

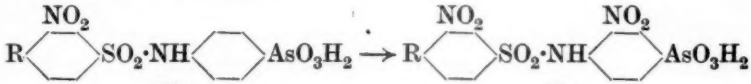
m-Nitrobenzenesulphonyl and *m*-nitro-*p*-toluenesulphonyl radicals have now been introduced into the amino-group of 4-aminophenylarsinic acid (I), and the former radical into the amino-groups of 3-amino-4-hydroxyphenylarsinic acid (II) and 4-amino-2-hydroxyphenylarsinic acid (III).



(I.) (II.) (III.)

For this purpose, the most convenient and by far the most effective method is a modification of the Schotten-Baumann method devised by Fischer and Bergell (*Ber.*, 1902, **35**, 3779) for the preparation of the β-naphthalenesulphonyl derivatives of amino-acids. The reaction with 3-amino-4-hydroxyphenylarsinic acid (II), an acid which is sensitive to caustic alkali, necessitates the use of sodium carbonate, and under these conditions a complex mixture results containing in all probability *O*-sulphonic esters and disulphonamides.

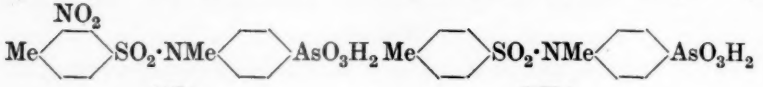
3′-Nitrobenzenesulphonyl- (IV; R = H) and *3′-nitro-4′-toluenesulphonyl-4-aminophenylarsinic acid* (IV; R = Me) on further nitration yield exclusively one dinitro-acid (V), the constitution following from the products of hydrolysis.



(IV.) (V.)

3′-Nitro-4′-toluenesulphonyl-4-methylaminophenylarsinic acid (VI), which is the methylation product of (IV; R = Me), was obtained by

the action of methyl sulphate and alkali at 100°. It was unobtainable by methylation at room temperature, although *4′-toluenesulphonyl-4-methylaminophenylarsinic acid* (VII) was readily formed under these conditions. The latter acid on solution in sulphuric acid at room temperature was completely hydrolysed and gave an



(VI.) (VII.)

80% yield of 4-methylaminophenylarsinic acid, an acid which is not new. This is, however, the best method for its preparation.

The seven nitro- and dinitro-arsinic acids aforementioned on reduction with ferrous chloride and alkali gave the corresponding amino-compounds quite smoothly and in good yield. When tested for trypanocidal activity on mice infected with *Trypanosoma equiperdum*, they were found to be without exception completely inactive on any dose, including the maximum tolerated, although in structure they differ from the active amides of previous communications only in the replacement of –CO·NH– by –SO_2·NH–. This is a surprising result. It might be ascribed to the presence of the strongly acidic hydrogen atom of the –SO_2·NH– group in comparison with that contained in the –CO·NH– group, but this was negatived by the inactivity of *3′-amino-4′-toluenesulphonyl-4-methylaminophenylarsinic acid* derived from (VI) by reduction. It is, however, possible to proceed a step further in the analysis of this anomaly.

Ehrlich first advanced the theory that the real active trypanocidal agent in arsenicals is the tervalent arsenic stage, basing it on the two groups of observations, that cures of small animals artificially infected with trypanosomes could be effected by primary quinquevalent arsinic acids and by the corresponding tervalent arseno-compounds and arsenious oxides, but *in vitro*, *i.e.*, outside the animal body, arsinic acids and arseno-compounds had negligible action on trypanosomes, whereas the oxides were very highly active. The view of the importance of the tervalent arsenious oxide has received further support from the experiments of Voegtlin and his associates in Washington, who show that animal tissues are able to reduce the arsinic acids and oxidise the arseno-compounds to the arsenious oxide stage :

$$R\cdot AsO_3H_2 \longrightarrow R\cdot AsO \longleftarrow R\cdot As{=}As\cdot R.$$

It was therefore of importance to test whether the oxides corresponding to the above-described inactive acids containing the sulphonamide group were trypanocidally active. *3′-Amino-4′-*

toluenesulphonyl- and 3 : 3′-*diamino*-4′-*toluenesulphonyl*-4-*aminophenylarsenious oxides* were prepared by reduction of the corresponding acids with sulphur dioxide and hydriodic acid, and the former oxide was examined in detail. It had a maximum tolerated dose of 0·01 mg. per g. of mouse, was thus twenty times as toxic as its parent acid and was completely devoid of trypanocidal activity on the infected animal, but at a dilution of 1 in 10,000 *in vitro* and 30 minutes' exposure, it rendered trypanosomes non-infective to the normal animal. As it can be calculated that this is just one-half the concentration which should obtain in the blood-stream of infected mice when injected intravenously with the maximum tolerated dose, it seems clear that the injected oxide must be de-activated by some body mechanism. Whatever be the ultimate chemical processes involved in the tissues which determine the distribution and fate of these acids or oxides before final excretion, it seems also certain that the sulphonamide linking must confer a general character on these molecules, independent of its orientation with respect to the arsinic acid group, which prevents the oxides from ever attaining a concentration inimical to the continued reproduction of the trypanosomes. Since the toxiphoric grouping is undoubtedly the group containing arsenic, the presence of the $-SO_2\cdot NH-$ group is reflected in an altered distribution of affinities around the arsenic atom. Some light might be thrown on this by precision measurements of the relative reduction potentials of arsinic acids containing the amide link and their analogues with the sulphonamide link.

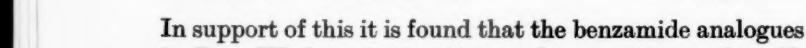
The *arseno*-compounds of 3′-*aminobenzenesulphonyl*-4-*aminophenylarsinic acid* and 3′-*amino*-4′-*toluenesulphonyl*-4-*aminophenylarsinic acid* are white, whereas the arseno-compounds of their benzamide analogues are orange and almost all previously recorded arseno-compounds are yellow or orange. The colour of arseno-compounds is usually ascribed to the presence of the chromophoric grouping –As=As– analogous to the azo-chromophore, –N=N–. The view might therefore be advanced that the loss of colour in the white arsenobenzenes is due to formation of a bimolecular complex.

$$\begin{matrix} R\cdot As{=}As\cdot R \\ R\cdot As{=}As\cdot R \end{matrix} \longrightarrow \begin{matrix} R\cdot As{-}As\cdot R \\ R\cdot As{-}As\cdot R \end{matrix}$$

Michaelis and Schäfer (*Ber.*, 1913, **46**, 1742) had found that the molecular weight of crystalline arsenobenzene and arsenotoluene in phenol as cryoscopic solvent agreed with the simple molecular weight. In the present instances, however, the experimental difficulties due to the peculiar properties of the substances have proved insurmountable.

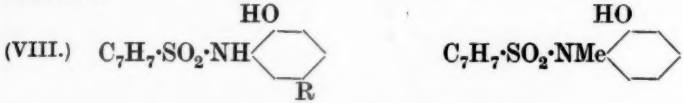
In connexion with some of the compounds described in this communication, the observation has been made that compounds containing a hydroxyl group ortho to a sulphonamide group give a striking series of colour reactions with iron, nickel, cobalt, and copper salts in sodium hydrogen carbonate solution, which are destroyed by excess of caustic alkali or free mineral acid. The cobalt solutions show an absorption band in the yellow-green parts of the spectrum. If a purple alkaline solution of the iron complex of *3′-aminobenzenesulphonyl-3-amino-4-hydroxyphenylarsinic acid*, for instance, be made neutral or weakly acid to litmus, a grey-black precipitate is formed, free from the anion of the precipitating acid, but with an iron–sulphur atomic ratio of approximately 1 : 1 and re-soluble in sodium hydrogen carbonate solution at least in part, with production of the original purple colour. The most reasonable view of the nature of the constituents of the coloured alkaline solutions is that a series of complex anions is formed analogous to the catechol complexes described by Weinland and Binder (*Ber.*, 1912, **45**, 148) and based, at least in the case of iron, on the ferricyanide or ferrioxalate model; but whereas the iron–catechol complexes are of a stability to alkali comparable with that of potassium ferricyanide, the iron–*o*-hydroxysulphonamide complexes seem to be of a stability probably inferior to that of the ferrioxalates.

On this view, the acidic hydrogen atoms of the $-SO_2\cdot NH-$ and $-OH$ groups enter into the co-ordination complex.



Ferricyanide. Catechol complex. *o*-OH sulphonamides.

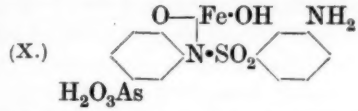
In support of this it is found that the benzamide analogues described in Part IV do not give these colour reactions, that *N-p*-toluenesulphonyl-*o*-aminophenol (VIII; R = H) and *toluenesulphonyl-3-amino-4-hydroxybenzoic acid* (VIII; R = CO_2H) give the colour reactions, but that N-p-*toluenesulphonyl*-o-*methylaminophenol* (IX) does not.



(VIII.) (IX.)

Incidentally Reverdin's so-called *O*-toluenesulphonyl-*N-p*-methylaminophenol (*Ber.*, 1909, **42**, 1523) has been shown to be *N*-toluenesulphonyl-*N-p*-methylaminophenol. The greyish-black precipitate previously mentioned as being obtained on acidification of the purple iron solutions possibly has the constitution (X) analogous to the ferric oxalohydroxamate (XI) of Hantzsch and Desch (*Annalen*,

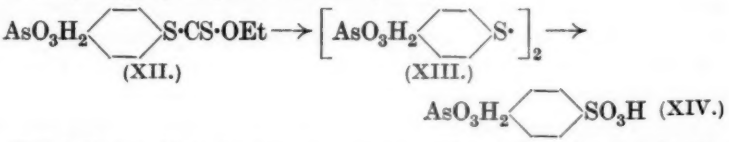
1902, **323**, 24), but development of the purple colour by solution of (X) in alkali cannot be mere formation of a soluble salt of the arsinic



acid grouping, because the same colour is obtained from (VIII; R = H), where the salt-forming group is absent.

4-Amino-2-hydroxyphenylarsinic acid (III), its 3′-*nitrobenzenesulphonyl*- and 3′-*aminobenzenesulphonyl*-derivatives also give colour reactions with ferric and cupric salts in sodium hydrogen carbonate solution. It is possible that in these cases also co-ordination compounds, involving the arsinic acid and adjacent hydroxyl groups, are formed.

In this communication it is convenient to incorporate some observations on one of the simplest aromatic arsinic acids containing the sulpho-group, namely, p-*sulphophenylarsinic acid*. In 1919, one of the authors (K.) made an unsuccessful attempt to prepare the thiol analogue of salvarsan, and the experiments which follow arose out of that attempt. *p*-Aminophenylarsinic acid was converted into p-*xanthylphenylarsinic acid* (XII) by Leuckardt's method (*J. pr. Chem.*, 1890, **41**, 179) and this on oxidation on the boiling water-bath with 3*N*-nitric acid gave a mixture of the sparingly soluble *diphenyl disulphide* pp′-*diarsinic acid* (XIII) and the extremely soluble p-*sulphophenylarsinic acid* (XIV).



The latter acid is, however, more readily obtained by oxidation of the disulphide by boiling 6*N*-nitric acid. The disulphide and the sulpho-acid proved to be devoid of trypanocidal action. The sulpho-acid was converted into the corresponding *arseno-acid* by reduction with hypophosphorous acid, but owing to its very ready solubility in water this could not be isolated sufficiently pure for physiological testing. Dr. Voegtlin has also prepared this sulpho-acid and its arseno-derivative (*Physiological Reviews*, 1925, **5**, 91), but he informed us verbally that his method for the preparation was different from ours.

We are indebted to Miss F. M. Durham and Miss J. Marchal of this department for the painstaking care with which they have determined the toxicities and trypanocidal action of the compounds described in this paper.

EXPERIMENTAL.

4′-Toluenesulphonyl-4-aminophenylarsinic Acid.—This acid, briefly described by Little, Cahen, and Morgan (J., 1909, **95**, 1482) as being obtained by the Schotten–Baumann reaction, may be obtained in 74% yield by the Fischer–Bergell method of arylsulphonylation. Sodium *p*-aminophenylarsinate pentahydrate (1 mol.) dissolved in 5 parts of water was shaken with finely-powdered *p*-toluenesulphonyl chloride (2 mols.) and a few drops of ether for 30 minutes. *N*-Sodium hydroxide (1 mol.) was then added, and the mixture again shaken for 30 minutes. This sequence was repeated until 3 molecular proportions of *N*-alkali had been added. The arsinic acid obtained on acidification was sparingly soluble in boiling water, crystallising in microscopic rectangular plates, but readily soluble in boiling 90% formic acid, crystallising therefrom in needles and diamond-shaped plates.

4′-Toluenesulphonyl-4-methylaminophenylarsinic Acid (VII).—4′-Toluenesulphonyl-4-aminophenylarsinic acid (1 mol.) was dissolved in 2*N*-sodium hydroxide (2 mols.) and heated in the boiling water-bath with vigorous stirring while methyl sulphate (16 mols.) and an equivalent quantity of 2*N*-sodium hydroxide were run in simultaneously, the reaction of the fluid being faintly alkaline throughout. On acidification a 90% yield of the methylated acid was obtained. It is readily soluble in boiling water and crystallises in needles which are unstable and pass readily into large, hexagonal plates. From alcohol it crystallises in needles and from 90% formic acid, in which it is extremely readily soluble, in microscopic, rectangular plates (Found: S, 8·0. $C_{14}H_{16}O_5NSAs$ requires S, 8·3%). This acid can also be obtained by methylation at room temperature.

4-Methylaminophenylarsinic Acid.—*p′*-Toluenesulphonyl-4-methylaminophenylarsinic acid was dissolved in 3½ volumes of concentrated sulphuric acid at room temperature, kept for 30 minutes, and then poured on to ice. The mixture having been made neutral to Congo paper, an 80% yield of *N*-methylaminophenylarsinic acid was obtained (Found: As, 32·6. Calc.: As, 32·4%). It is very soluble in *N*-hydrochloric acid and with nitrite gives an instant precipitate of fine needles of the nitroso-compound. On slight dilution, these rapidly transform into six-sided plates which give the Liebermann nitroso-reaction. This acid had a tolerated dose of 0·05 mg. per g. of mouse, and on this dose mice infected with *T. equiperdum* relapsed in the most favourable cases within 7 days.

Sodium 3-Nitro-4-toluenesulphonate.—The following process is an improvement on that of Otto and Gruber (*Annalen*, 1868, **145**, 23)

and of Fichter and Bernouilli (*Ber.*, 1909, **42**, 4309). *p*-Toluenesulphonic acid (100 g.) was heated with 380 c.c. of nitric acid (*d* 1·42) in the boiling water-bath for 30 minutes. The solution was poured into a litre of water and rapidly evaporated to dryness under reduced pressure. The residue, which crystallised in envelope-shaped plates, was re-evaporated with small quantities of water to remove all nitric acid, and the solution then neutralised with sodium carbonate. On concentration, a 72% yield of the *monohydrated sodium* salt was obtained (Found: Loss at 100°, 7·3. $C_7H_6O_5NSNa,H_2O$ requires H_2O, 7·0%. Found on dried salt: Na, 9·9. $C_7H_6O_5NSNa$ requires Na, 9·6%). The *barium* salt, which is less soluble than the sodium salt and crystallises in creamy, glistening leaflets, was prepared by addition of barium chloride to a solution of the sodium salt (Found: Loss at 100°, 6·2. $C_{14}H_{12}O_{10}N_2S_2Ba,2H_2O$ requires H_2O, 6·0%. Found on dried salt: Ba, 24·3. $C_{14}H_{12}O_{10}N_2S_2Ba$ requires Ba, 24·1%).

In another experiment using 15 g. of acid and 50 c.c. of nitric acid, the solution obtained on pouring the product into water was extracted thrice with ether. The ethereal extract was freed from acids by extraction with alkali and on evaporation gave 0·75 g., a 6·3% yield, of *p*-nitrotoluene. The main bulk melted at 54°, as did a mixture with pure *p*-nitrotoluene, but a trace melted 10° higher, suggesting the presence of 2 : 4-dinitrotoluene.

3′-Nitro-4′-toluenesulphonyl-4-aminophenylarsinic Acid (IV; R = Me).—Sodium *p*-aminophenylarsinate was submitted to the action of *m*-nitro-*p*-toluenesulphonyl chloride (2 mols.) by the Fischer–Bergell process described above. The yield of required acid was 77%. It is sparingly soluble in boiling water and crystallises therefrom in minute, rectangular plates (Found: S, 7·8. $C_{13}H_{13}O_7N_2AsS$ requires S, 7·7%). The maximum tolerated dose for mice is 0·3 mg. per g. of mouse and subsequent toxicities are expressed on the same basis.

3′-Nitro-4′-toluenesulphonyl-4-methylaminophenylarsinic Acid (VI).—This acid was obtained in 93% yield by methylation of the preceding acid by the process described for its analogue without the nitro-group. It is not formed in recognisable quantity by methylation at room temperature, using a large excess of methyl sulphate and a variety of concentrations of potassium or sodium hydroxide. It is soluble in 200 parts of boiling water and crystallises in feathery needles, but from alcohol in large, hexagonal plates and from 90% formic acid in diamond-shaped plates (Found: S, 7·3. $C_{14}H_{15}O_7N_2SAs$ requires S, 7·4%). The maximum tolerated dose is 0·03 mg.

3′-Amino-4′-toluenesulphonyl-4-aminophenylarsinic Acid.—The nitro-acid (8·3 g.) was reduced with ferrous chloride and alkali as

described in previous papers of this series. The alkaline extracts (0·2*N*-NaOH) of the ferric hydroxide precipitate were neutralised to Congo-paper, and the crystalline amino-acid which separated was kept over-night. It was collected, dissolved in 140 c.c. of *N*-hydrochloric acid at 50°, and when precipitated by careful addition of saturated sodium acetate separated in small, prismatic needles. The first precipitation mother-liquors treated at 100° with ammonia and magnesium chloride gave a small quantity of *magnesium* salt which gave a further small proportion of the required amino-acid. The total yield was 73% (Found: S, 8·3. $C_{13}H_{15}O_5N_2SAs$ requires S, 8·3%). This *amino-acid* is readily soluble in 2*N*- or 3*N*-mineral acids, the *hydrochloride* being precipitated in small, oblique rhombs by concentrated hydrochloric acid. The maximum tolerated dose is 0·2 mg.

3′-*Amino*-4′-*toluenesulphonyl*-4-*aminophenylarsenious Oxide*.—The foregoing acid (1·8 g.) was dissolved in 10·8 c.c. of water with the aid of 8·2 c.c. of concentrated hydrochloric acid. On addition of 0·45 g. of potassium iodide in a few drops of water there was rapid separation of iodine and a brown gum, but on passing sulphur dioxide for successive ½-hour intervals with intermediate kneading of the now pale yellow gum, it eventually crystallised completely in almost quantitative yield. It was titrated by Ehrlich and Bertheim's method for *p*-aminophenylarsenious oxide (*Ber.*, 1910, **43**, 917) (Found: 0·2185 g., dry, required 9·02 c.c. of *N*/10-iodine. Calc. for $C_{13}H_{13}O_3N_2SAs$: 9·06 c.c.). The agreement is fortuitous, as the product contained hydrochloride. It was dissolved in water, and the free *oxide* precipitated as a white, amorphous powder by addition of sodium hydrogen carbonate (Found: 0·2132 g. equiv. to 11·53 c.c. of *N*/10-iodine. Calc.: 12·04 c.c. Whence the purity was 96%). This arsenious oxide reduces ammoniacal silver solution only on warming. It is readily soluble in *N*-hydrochloric acid and diazotises and couples in the usual way. It is also readily soluble in 0·5*N*-sodium carbonate and 2*N*-ammonia but not in sodium hydrogen carbonate.

3′-*Aminotoluenesulphonyl*-4-*aminoarsenobenzene*.—The foregoing arsenious oxide (1·25 g.) was dissolved in water (6 c.c.) with addition of 6 c.c. of hypophosphorous acid (*d* 1·137) and a crystal of potassium iodide. The solution was stirred and the temperature slowly raised to 80°. The arsenobenzene separated in microscopic needles which were centrifuged off, washed first with water and then with sodium hydrogen carbonate solution, and finally with several changes of water. The crystalline character was retained throughout. The yield was 1·1 g. The same compound was also obtained in the crystalline state very readily by reduction of the corresponding acid

at 50—55° (Found : 0·1158 g. required 13·9 c.c. of *N*/10-iodine in the presence of sodium acetate. Calc. : 13·7 c.c. Found : As, as $Mg_2As_2O_7$, 22·6. $C_{26}H_{26}O_4N_4As_2S_2$ requires As, 22·3%). This arseno-compound is white or of a pale cream colour. It is readily soluble in molten phenol, but insoluble in acetic acid. It is insoluble in mineral acids, but dissolves on addition of nitrite and then couples in the usual way. It dissolves in an equivalent amount of sodium hydroxide, but is precipitated as the sodium salt by a slight excess. It is also slowly soluble in sodium carbonate solution. The dried powder is very easily electrified and consequently very difficult to handle. The maximum tolerated dose is 0·1 mg.

3′-Amino-4′-toluenesulphonyl-4-methylaminophenylarsinic Acid.—This acid was obtained in 75·3% yield by reduction of the corresponding nitro-acid with ferrous chloride and alkali. It was purified by solution in *N*-hydrochloric acid and precipitation by sodium acetate (Found : S, 8·1. $C_{14}H_{17}O_5N_2SAs$ requires S, 8·0%). This acid crystallises readily from boiling water in clusters of thin plates. It is readily soluble in warm *N*-hydrochloric acid, the *hydrochloride* crystallising in prisms. The *sulphate* and *nitrate* are sparingly soluble in their respective *N*-acids and both crystallise in fine needles. The maximum tolerated dose is 0·03 mg.

3 : 3′-Dinitro-4′-toluenesulphonyl-4-aminophenylarsinic Acid (V; R = Me).—This acid was prepared in 73% yield from 8·3 g. of 3′-nitrotoluenesulphonyl-4-aminophenylarsinic acid, dissolved in 25 c.c. of sulphuric acid and nitrated with 2 g. of nitric acid (*d* 1·42) in 2 g. of sulphuric acid. It crystallises from boiling water, in which it is sparingly soluble, in very small needles, and from glacial acetic acid, in which it is moderately soluble, in bunches of small, prismatic needles (Found : S, 6·9. $C_{13}H_{12}O_9N_3SAs$ requires S, 6·9%). The maximum tolerated dose is 0·1 mg.

3 : 3′-Diamino-4′-toluenesulphonyl-4-aminophenylarsinic Acid.—This acid was prepared by reduction of the preceding dinitro-acid (9·2 g.) with ferrous chloride and alkali. The alkaline extracts of the ferric hydroxide gave 2·7 g. of acid by direct precipitation and 2·0 g. by way of the *magnesium* salt in hot ammoniacal solution. The total yield was 60%. This *diamino-acid*, precipitated from acid solution by sodium acetate, separates in small, rhomb-shaped plates. It is very soluble in dilute mineral acids and diazotises and couples with alkaline β-naphthol with a blood-red colour (Found : As, 18·9. $C_{13}H_{16}O_5N_3SAs$ requires As, 18·7%). The maximum tolerated dose is 0·5 mg.

3 : 3′-Diamino-4′-toluenesulphonyl-4-aminophenylarsenious Oxide.—One g. of the preceding acid was dissolved in 4·5 c.c. of con-

centrated hydrochloric acid and 6 c.c. of water. Potassium iodide (0·25 g.) was added and sulphur dioxide passed for an hour. A crystalline salt separated in long, yellow needles (Found for anhydrous material : 0·1138 g. equiv. to 3·57 c.c. of *N*/10-iodine. Calc. for the pure dihydriodide : 3·97 c.c.). The remainder was dissolved in water, and the oxide precipitated with sodium hydrogen carbonate. The yield was 0·4 g. (Found for anhydrous oxide : 0·1623 g. equiv. to 8·41 c.c. of *N*/10-iodine. $C_{13}H_{14}O_3N_3SAs$ requires 8·84 c.c. Hence the purity was 95%).

3′-Nitrobenzenesulphonyl-4-aminophenylarsinic Acid (IV ; R = H). —This acid was prepared from sodium *p*-aminophenylarsinate (1 mol.) and finely powdered nitrobenzenesulphonyl chloride (2 mols.) by the Fischer–Bergell method. The yield was 69% (Found : S, 7·7. $C_{12}H_{11}O_7N_2SAs$ requires S, 8·0%). It is soluble in boiling 90% formic acid, and crystallises in short prisms, less readily in boiling acetic acid and very sparingly in boiling water. The maximum tolerated dose is 0·4 mg.

3′-Aminobenzenesulphonyl-4-aminophenylarsinic Acid.—The corresponding nitro-acid was reduced by ferrous chloride and alkali in the usual way at 0°, and the amino-acid isolated through its *magnesium* salt in hot ammoniacal solution. The yield was 70%. It is best purified as its *hydrochloride*, which is only moderately soluble in cold water and separates readily on addition of stronger acid in rhomb-shaped plates (Found : Cl, 8·5. $C_{12}H_{13}O_5N_2SAs,HCl$ requires Cl, 8·7%). On addition of saturated sodium acetate solution to a warm concentrated solution of the hydrochloride, the *aminoarsinic acid* separates as a gum which rapidly crystallises, on rubbing, in long, narrow plates with sloping ends. It is moderately soluble in cold water. The maximum tolerated dose is 0·5 mg.

3′-Aminobenzenesulphonyl-4-aminoarsenobenzene.—This was prepared from the corresponding acid by means of hypophosphorous acid at 45—50° in the usual way (Found : As, 23·6. $C_{24}H_{22}O_4N_4S_2As_2$ requires As, 23·3%). It is a white or creamy-white, amorphous powder when dry, soluble in sodium hydroxide, and slowly soluble in sodium carbonate solution. It dissolves in molten phenol, but the solution soon becomes turbid and finally fills with a finely-divided precipitate.

3 : 3′-Dinitrobenzenesulphonyl-4-aminophenylarsinic Acid (V ; R = H).—3′-Nitrobenzenesulphonyl-4-aminophenylarsinic acid (10·0 g.) in 30 c.c. of sulphuric acid was slowly treated at 0° with nitric acid (1·75 c.c. ; *d* 1·42) dissolved in a little sulphuric acid (5 c.c.). After 30 minutes, the solution was poured on to ice. The yield was 93%. This *dinitro-acid* crystallises well from boiling water, in which it is sparingly soluble, in short needles and similarly

from boiling 90% formic acid, in which it is readily soluble (Found: S, 7·2. $C_{12}H_{10}O_9N_3SAs$ requires S, 7·2%). On boiling with 32% hydrochloric acid for 8 hours, it was only partly hydrolysed, giving an 83% yield of 3-nitro-4-aminophenylarsinic acid. No 4-aminophenylarsinic acid could be detected in the mother-liquors. The maximum tolerated dose is 0·1 mg.

3 : 3′ - *Diaminobenzenesulphonyl* - 4 - *aminophenylarsinic Acid.*—Reduction of the corresponding dinitro-acid by ferrous chloride and alkali at 0° gave this *diamino-acid* in 70% yield. It was isolated through the magnesium salt in ammoniacal solution (Found: As, 19·5. $C_{12}H_{14}O_5N_3SAs$ requires As, 19·4%). When liberated from acid solution by addition of sodium acetate, it crystallises in slightly distorted, diamond-shaped plates. The maximum tolerated dose is 1·5 mg.

3′-*Nitrobenzenesulphonyl*-3-*amino*-4-*hydroxyphenylarsinic Acid.*—3-Amino-4-hydroxyphenylarsinic acid (11·6 g.) was dissolved in water (60 c.c.) with the aid of 3·85 g. of anhydrous sodium carbonate. Nitrobenzenesulphonyl chloride (2 mols.; 22 g.) was added at once and a few drops of ether. The mixture was shaken for 30 minutes, and three successive portions of *N*-sodium carbonate (1 mol.) at 30-minute intervals were then added with intermediate shaking. The solution, on being made definitely acid to Congo-paper, deposited a pale-coloured gum immediately and, after 12 hours in the cold room, a crystalline powder. These were collected and stirred with 75 c.c. of *N*-hydrochloric acid in the boiling water-bath until the non-soluble portion had crystallised. This treatment was essential to remove aminohydroxyphenylarsinic acid carried down from acid solution with the gum. The crystalline, chalky solid obtained on cooling was a complex mixture probably containing *O*- and di-*N*-sulphonylated derivatives (Found: S, 9·0. A disulphonamide requires S, 10·6%). It was dissolved in 20 volumes of 0·5*N*-sodium hydroxide, boiled for 30 minutes, and while still hot treated with concentrated hydrochloric acid so long as an oily turbidity was produced. After brief stirring, the hot solution was freed from oil by filtration through a fluted paper. The filtrate showed no further tendency to deposit oil, but deposited the required nitro-acid in a crystalline state. The original mother-liquors on concentration under reduced pressure gave a succession of crops of the required nitro-acid and unchanged aminohydroxyphenylarsinic acid separable by extraction with *N*-hydrochloric acid. The total yield was 33%. If one molecular proportion of sulphonyl chloride was originally used instead of two, the same difficulties were encountered and the yield was 28%. For analysis, the *acid* was recrystallised from 20 volumes of boiling water, from which it crystallised extremely well

as a *dihydrate* in large, straw-coloured prisms or rhombs (Found : Loss at 95°, 8·4. $C_{12}H_{11}O_8N_2SAs,2H_2O$ requires H_2O, 7·9%. Found on anhydrous material : S, 8·0. $C_{12}H_{11}O_8N_2SAs$ requires S, 7·7%). When dissolved in sodium hydrogen carbonate solution and treated with a drop of dilute ferric chloride, it gives an intense purple solution which on addition of caustic alkali becomes redder; the colour is discharged by excess of caustic alkali with separation of ferric hydroxide. On addition of acid, however, to neutrality to litmus, the colour is also discharged with precipitation of a grey, amorphous precipitate which, after separation, redissolves in sodium hydrogen carbonate solution with the same purple colour. In a similar way, cobalt nitrate gives a rose-coloured solution with an absorption band in the yellowish-green part of the spectrum. The reaction is more intense in sodium carbonate solution, but is discharged by excess of acid or caustic alkali. A nickel salt gives a clear yellowish-brown solution, whilst a copper salt gives an intense deep brown solution. The maximum tolerated dose is 0·5 mg.

3′-Aminobenzenesulphonyl-3-amino-4-hydroxyphenylarsinic Acid.—The reduction of the foregoing nitro-acid was carried out with ferrous chloride and alkali. The isolation of the pure amino-acid was effected as follows. The filtrate from the ferric hydroxide together with the alkaline extracts (0·2*N*-sodium hydroxide) of the ferric hydroxide was of a deep purple colour, and on being made neutral to Congo-paper deposited, after standing for 12 hours, the required amino-acid mixed with an amorphous, grey complex of ferric hydroxide and the amino-acid. These were collected, dissolved in 2*N*-sodium hydroxide, and filtered from the ferric hydroxide, which separated in part. The filtrate, on being made neutral to litmus, deposited the remainder of the bound iron as the complex, which could be removed, and thereafter the pure amino-acid was obtained on making the filtrate neutral to Congo-paper. The iron complex could be re-submitted to the same treatment with caustic alkali, when ferric hydroxide was again precipitated, but not quite completely, and the filtrate gave a further small crop of iron complex and the pure amino-acid on being made neutral to litmus and Congo-paper, respectively. The original mother-liquors, on concentration under reduced pressure, yielded further crops of pure amino-acid. For physiological testing and analysis, the combined crops of amino-acid were dissolved in *N*-hydrochloric acid and precipitated with saturated sodium acetate solution. The yield was 76% (Found : Loss at 95°, 7·5; S, 7·5. $C_{12}H_{13}O_6N_2SAs,2H_2O$ requires H_2O, 8·1; S, 7·6%). It crystallises from boiling water, in which it is fairly readily soluble, in glistening prisms. It is readily soluble in *N*-hydro-

chloric, nitric, or sulphuric acid. The *hydrochloride* crystallises in rectangular tablets, the *sulphate* in short needles, and the *nitrate* in prisms. In sodium hydrogen carbonate solution, the amino-acid gives a purple colour with ferric chloride and on neutralisation to litmus a complex containing iron is precipitated as a dove-grey powder. Some preparations, however, are almost black. This is free from chloride and dissolves in sodium hydrogen carbonate with restoration of the purple colour (Found on air-dried material: Fe, 10·4; S, 6·5, whence Fe : S = 1 : 1·08). The rose-pink colour developed on similar addition of cobalt nitrate is very marked. There is an absorption band in the yellowish-green. A soluble nickel complex is similarly formed with a yellowish-brown colour, and with copper salts a very intense brownish-red solution is obtained showing considerable stability to caustic alkali. The maximum tolerated dose is 0·5 mg.

3′-Nitrobenzenesulphonyl-4-amino-2-hydroxyphenylarsinic Acid.—4-Amino-2-hydroxyphenylarsinic acid (11·6 g.) was converted into the sulphonamide by the Fischer–Bergell process, nitrobenzenesulphonyl chloride (2 mols.) being used. The solution, on being made acid to Congo-paper, deposited a gum and, on standing some hours, a crop of crystals. The total precipitate was collected and warmed on the water-bath with *N*-hydrochloric acid; it then became wholly crystalline. It was dissolved in 10 volumes of *N*-sodium hydroxide and heated on the water-bath for 30 minutes. The *nitro-acid* was obtained on acidification in colourless needles rapidly transforming to plates; yield 9·1 g. The original mother-liquors contained additional acid, which was isolated by concentration. This acid is a dihydrate (Found: Loss at 95°, 8·4. $C_{12}H_{11}O_8N_2SAs,2H_2O$ requires H_2O, 8·2%. Found on anhydrous material: S, 8·0, 7·6. $C_{12}H_{11}O_8N_2SAs$ requires S, 7·7%). It is soluble in 32 parts of boiling water and separates in very pale buff-coloured rhombs or prisms. (For its colour reactions, see next paragraph.) The maximum tolerated dose is 0·2 mg.

3′-Aminobenzenesulphonyl-4-amino-2-hydroxyphenylarsinic Acid.—This acid was prepared from the nitro-acid in 63% yield by means of ferrous chloride and alkali. It tends to form an iron complex in the alkaline extracts of the ferric hydroxide precipitate just as does its isomeride described above. It can be isolated, however, in exactly the same way (Found: S, 8·1. $C_{12}H_{13}O_6N_2SAs$ requires S, 8·3%). It is readily soluble in boiling water and crystallises in tufts of fine needles. In *N*-mineral acids it is very readily soluble. When dissolved in sodium hydrogen carbonate solution, it gives a clear deep yellowish-brown colour with ferric chloride and a bright emerald-green colour with copper sulphate. Under comparable

conditions, the parent nitro-acid gives with ferric chloride a clear reddish-brown solution and with copper salts an olive-green solution. The parent acid of this group, 4-amino-2-hydroxyphenylarsinic acid, gives a reddish-brown solution with ferric salts and an emerald-green solution with copper sulphate. The maximum tolerated dose is 0·025 mg.

N-p-*Toluenesulphonyl*-o-*aminophenol* (VIII; R = H).—When prepared by the process described by Reverdin and de Luc (*Ber.*, 1914, **47**, 1538) for the isomeric derivative of *m*-aminophenol, this sulphonamide was obtained in very good yield and agreed in properties with the description given by Tröger and Ullmann (*J. pr. Chem.*, 1895, **51**, 441). It dissolves on warming with dilute aqueous sodium carbonate; the solution becomes turbid on cooling and gives a bright purple colour on addition of ferric chloride. With cobalt nitrate, it gives a pink colour with an absorption band in the yellow-green.

N-p-*Toluenesulphonyl*-o-*methylaminophenol* (IX) was prepared by extending Reverdin and de Luc's method to *o*-methylaminophenol. *o*-Methylaminophenol sulphate (" Ortol," 4·3 g.) and sodium acetate (6·8 g.; hydrated) were dissolved in 50% alcohol (100 c.c.) and heated for 30 minutes on the water-bath, *p*-toluenesulphonyl chloride (4·75 g.) being added in several portions from time to time. On cooling, N-p-*toluenesulphonyl*-o-*methylaminophenol* (4·6 g.) separated in white needles. It was recrystallised from glacial acetic acid and showed m. p. 127—128° (Found: S, 11·3. $C_{14}H_{15}O_3NS$ requires S, 11·6%). It is readily soluble in caustic alkali but insoluble in dilute acids. It is unchanged by nitrous acid. Its solution in boiling dilute aqueous sodium carbonate becomes turbid on cooling, but gives no purple colour with ferric chloride and no pink colour with cobalt nitrate.

N-4-*Toluenesulphonyl*-3-*amino*-4-*hydroxybenzoic Acid* (VIII; R = CO_2H).—Aminohydroxybenzoic acid (1·5 g.) was dissolved in 10 c.c. of pyridine and treated with 2·37 g. of toluenesulphonyl chloride. After 12 hours, the mixture was poured into *N*-hydrochloric acid, the solid collected, and boiled for 30 minutes with *N*-sodium hydroxide. On acidification the sulphonamide separated straightway almost pure in 77% yield. For analysis it (2·3 g.) was recrystallised from the minimum volume (50 c.c.) of 50% (by vol.) acetic acid and separated in glistening, pale straw-coloured, wedge-shaped prisms, m. p. 250° (decomp.) (Found: S, 10·7. $C_{14}H_{13}O_5NS$ requires S, 10·4%). In sodium hydrogen carbonate solution it gives an intense purple colour with ferric chloride and a bright pink colour with cobalt nitrate, the solution showing an absorption band in the yellowish-green part of the spectrum.

N-p-*Toluenesulphonyl*-p-*methylaminophenol* was prepared following Reverdin's directions for his so-called *O*-toluenesulphonyl-*N*-*p*-monomethylaminophenol. It melts at 136—137° (Reverdin gives 135°) and crystallises in needles from dilute alcohol or benzene. It is insoluble in dilute acids and unchanged by nitrous acid, but is readily soluble in sodium hydroxide and in sodium carbonate solution on warming. When dissolved in sodium carbonate solution, it does not give a coloration with ferric chloride.

p-*Xanthylphenylarsinic Acid* (XII).—Sodium *p*-aminophenylarsinate pentahydrate (32·9 g.) was diazotised at 0° in 200 c.c. of water and 30 g. of concentrated hydrochloric acid, and the product run slowly into a rapidly stirred solution of 20 g. of potassium xanthate in 420 c.c. of a 10% solution of hydrated sodium carbonate, kept at 80°. After being stirred for 1 hour, the solution was cooled and acidified. The precipitated resin solidified after a few hours and was submitted to a partial purification by dissolution in sodium carbonate solution, filtration from insoluble by-products, and reprecipitation by acids. The yield of crude xanthate was 62% (Found: S, 18·8. $C_9H_{11}O_4S_2As$ requires S, 19·9%). The acid could not be obtained crystalline nor of a higher sulphur content, but it behaved normally on oxidation.

Oxidation of p-*Xanthylphenylarsinic Acid*.—Five g. of crude *p*-xanthylphenylarsinic acid were heated on the water-bath for 2 hours with 100 c.c. of 3*N*-nitric acid and finally to boiling for ½ hour. When cold, the crystalline acid was collected (yield 82%). *Diphenyl disulphide* pp'-*diarsinic acid* (XIII) dissolves in 900 parts of boiling water, from which it crystallises in narrow plates or needles. It crystallises much more readily from 200 parts of 2*N*-nitric acid (Found: As, 32·2; S, 13·9. $C_{12}H_{12}O_6S_2As_2$ requires As, 32·2; S, 13·8%). A 1% solution in 0·2*N*-ammonia treated with 5% barium chloride solution gave, on heating, a *barium* salt crystallising in needles. On cooling, the barium salt rapidly re-dissolved, but was again precipitated on heating. The acid has a maximum tolerated dose of 0·002 mg.

The nitric acid mother-liquors of the above oxidation were evaporated to a syrup with repeated additions of water to remove the excess of nitric acid. They were then diluted and treated with sufficient baryta to precipitate the sulphuric acid present. On evaporation the solution set to a crystalline magma of p-*sulphophenylarsinic acid* (XIV). This was redissolved in water, and the solution evaporated until a crust formed. On keeping, the acid separated in long prisms. These are extremely soluble in water, but can be freed from the mother-liquors by washing with glacial acetic acid. The whole of the *p*-xanthylphenylarsinic acid unaccounted

for as disulphide appears to be present as sulpho-acid. The sulpho-acid was, however, more readily obtained as follows. The disulphide (5 g.) was boiled with 50 c.c. of 6*N*-nitric acid for 4 hours. The clear solution was evaporated dry and left 6·0 g. of crude sulpho-arsinic acid. This was crystallised once from water and washed with glacial acetic acid (Found: Loss at 95°, 5·8. $C_6H_7O_6SAs,H_2O$ requires H_2O, 6·0%. Found on anhydrous material: S, 11·6. $C_6H_7O_6SAs$ requires S, 11·4%). This acid also crystallises occasionally in hexagonal plates, possibly an anhydrous form, as it frequently appears as a crust on the surface of hot saturated solutions. The maximum tolerated dose is 0·5 mg.

The disulphide is reduced by hypophosphorous acid in the presence of a trace of iodide to an insoluble, yellow arseno-compound, probably *thiolarsenobenzene*, because it is insoluble in sodium hydrogen carbonate but soluble in caustic alkali. Under similar conditions, at 50—55° *p*-sulphophenylarsinic acid is reduced to p-*sulphophenylarsenobenzene*, which is very soluble in water and can be isolated in a crude condition as a yellow, gelatinous product by evaporation of the reduction liquors in a vacuum over sulphuric acid.

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CLXXVII.—*The Action of Phosphorus on Salts of Silver and Other Metals.*

By OSWALD JAMES WALKER.

IT has long been known that yellow phosphorus is able to precipitate many heavy metals from solutions of their salts, and attempts have been made to obtain quantitative information about the phenomenon by determining the ratio of metal deposited to phosphorus which had reacted. Using solutions of copper sulphate, Straub (*Z. anorg. Chem.*, 1903, **35**, 460) investigated the ratio of the amount of copper deposited to the total amount of phosphorus which had reacted (*i.e.*, phosphorus as phosphide and phosphoric acid), but he did not obtain any definite value. He concluded that the action proceeded in stages, and that when it was incomplete or when atmospheric oxygen was rigorously excluded 1 atom of phosphorus precipitated 2 atoms of copper. Tauchert (*Z. anorg. Chem.*, 1913, **79**, 350) obtained similar results, but stated that hypophosphoric acid was one of the products. Bird and Diggs (*J. Amer. Chem. Soc.*, 1914, **36**, 1382) also investigated the action of phosphorus on copper sulphate and concluded that the main

action consisted in the transfer of positive charges from the copper ions to the phosphorus, as follows :

$$5Cu^{\cdot\cdot} + 2P = 2P^{\cdot\cdot\cdot\cdot\cdot} + 5Cu,$$

the positive phosphorus ions reacting immediately with water to form phosphoric acid. In support of their theory, Bird and Diggs found that the ratio of atoms of copper precipitated to phosphorus oxidised to phosphoric acid was approximately 5 : 2. In obtaining this ratio, however, they did not include the amount of phosphorus present as lower acids and as phosphide. They ascribed these products to secondary reactions.

Experimental.

In order to determine to what extent phosphorus reacts with solutions of salts of the heavy metals and to decide which metal would be most suitable for a more detailed investigation, sticks of phosphorus were kept in contact with solutions of salts of a large number of different metals. Deposits of metallic appearance were found on the surface of the phosphorus after varying intervals with neutral or slightly acid solutions of salts of the following metals—gold, platinum, palladium, silver, mercury, and copper. No action was observed, even after several weeks, with salts of metals below copper in the electrochemical series, provided that the solution was not alkaline. In ammoniacal solution, however, salts of the following metals also gave deposits on the surface of the phosphorus—lead, nickel, thallium, and, not quite so readily, tin, cobalt, cadmium, and zinc. An interesting point of considerable importance is revealed by comparing these results with the data which are available for the action of phosphine on metallic salt solutions in papers by Kulisch (*Annalen*, 1885, **231**, 327), Moser and Brukl (*Z. anorg. Chem.*, 1922, **121**, 73), and Brukl (*ibid.*, 1922, **125**, 252). An examination of their results shows that those solutions which react with phosphine are exactly those which give deposits on phosphorus, and the metals may be divided into the same two groups mentioned above with respect to the action of phosphine on their salt solutions. Reference to this point will be made at a later stage.

From the above experiments, the most suitable salts for a more detailed investigation seemed to be those of silver and copper. As silver salts had not been used previously in any quantitative study, it was decided to examine more closely the action of phosphorus on them and especially on the nitrate. There is no possibility in this case of the metal being reduced to a lower stage of valency, and, as will be shown below, the complications due to the

formation of phosphide are not so great as with copper salts. In order to minimise any oxidising effect due to the free nitric acid formed, concentrations not greater than $N/10$ were used as a rule.

Action of Yellow Phosphorus on Silver Salts.

The phosphorus used throughout the course of this work was purified by warming with caustic soda solution, then with potassium dichromate and sulphuric acid, followed by thorough washing. It was cast into thin sticks and kept under water in the dark.

When a stick of phosphorus was placed in a $N/10$-solution of silver nitrate, a black, shiny deposit was formed almost immediately on the surface of the phosphorus; bright crystalline silver was then slowly deposited which finally became grey and spongy when it was all out of solution. After complete deposition of the silver, the solution contained phosphoric, phosphorous, and nitric acids, and traces of nitrous acid. No hypophosphorous acid, hypophosphoric acid, or ammonia was detected. The deposit consisted almost entirely of metallic silver, but contained a small amount of phosphorus, due to a thin, darker layer next to the surface of the phosphorus stick. This thin layer appeared to be a phosphide of silver and was probably the same as the black deposit first formed when the phosphorus was placed in the silver nitrate solution. The amount of phosphorus present in the deposit was small compared with that in the solution as oxy-acids. The question of phosphide formation will be considered later.

With solutions of silver sulphate and of silver acetate the reaction proceeded in a similar way. When phosphorus was placed in an ammoniacal solution of silver nitrate, a black deposit was formed which was converted, after some time, into white, crystalline silver. With a solution of silver cyanide in potassium cyanide a black deposit was very slowly formed on the surface of the phosphorus.

Quantitative Experiments with Silver Salts.—Experiments were made in the first place to determine whether any definite relationship existed between the amount of silver deposited and the total amount of phosphorus oxidised. Preliminary determinations showed that the ratio of the number of atoms of silver precipitated to the number of atoms of phosphorus oxidised, denoted hereafter as Ag : P, varied with the length of time during which the phosphorus had remained in contact with the solution. Accordingly, the ratio Ag : P was determined before complete precipitation of the silver had taken place.

Sticks of phosphorus were placed in solutions of silver nitrate, and portions withdrawn at intervals for the determination of the

amounts of silver salt and of phosphorus acids in the solution. The silver was determined in one portion by Volhard's method. A second portion was evaporated to dryness with aqua regia in order to ensure complete oxidation of the phosphorous acid, and the phosphoric acid was determined gravimetrically as magnesium pyrophosphate. In later experiments, this method was replaced by the more convenient volumetric method of Wilkie (*J. Soc. Chem. Ind.*, 1910, **29**, 794), in which the phosphoric acid was precipitated under given conditions as silver phosphate by means of standard silver nitrate solution, the excess of silver nitrate being titrated with thiocyanate solution after filtering.

TABLE I.

Expt.	$AgNO_3$.	Time (hrs.).	Ag pptd. ($= a$).	P oxid. ($= b$).	Ag : P ($= a/b$).	$\frac{a-a_0}{b-b_0}$.
1	0·1008	19	0·0279	0·00588	4·74	—
		48	0·0764	0·01810	4·22	4·0
		55	0·0904	0·02207	4·10	3·9
		61	0·1008	0·02836	3·55	—
2	0·1000	24	0·0190	0·00367	5·18	—
		48	0·0704	0·0156	4·51	4·3
		54	0·0846	0·0197	4·29	4·1
		59	0·0975	0·0236	4·13	3·9
		72	0·1000	0·0303	3·29	—
3	0·1000	16·5	0·0112	0·00204	5·49	—
		24	0·0210	0·00428	4·91	(4·4)
		41	0·0608	0·01419	4·29	4·1
		65	0·0996	0·02686	3·70	3·6
4	0·1000	16·5	0·0120	0·00243	4·94	—
		24	0·0228	0·00470	4·85	(4·8)
		41	0·0624	0·01472	4·24	4·1
		65	0·1000	0·02826	3·54	—
5	0·502	—	0·1060	0·0187	5·66	—
		—	0·1555	0·0305	5·09	4·2

The results of several experiments with solutions of silver nitrate are in Table I, all concentrations being given in g.-atoms or g.-mols. per litre. The general conclusions may be summarised as follows:

1. The ratio Ag : P varied during the deposition of the silver from a value of more than 5 : 1 near the beginning of the reaction to about 3·6 : 1 at the point corresponding to complete deposition of the silver.

2. No appreciable oxidation of the phosphorus by the oxy-acid set free from the metallic salt took place. Experiments in which solutions of the sulphate were used, in order to avoid the formation of nitric acid, gave results similar to those obtained with the nitrate solutions.

3. The phosphorus was not appreciably oxidised by atmospheric oxygen. Similar results were obtained whether air was bubbled through the solution (Expt. 3) or completely excluded (Expt. 4) during the deposition of the silver.

4. The oxygen necessary for the oxidation of the phosphorus must therefore come from the decomposition of the water.

A further slow oxidation of the phosphorus took place even after complete precipitation of the silver. This is shown by the results in Table II. In these experiments equal quantities of a standard silver nitrate solution were sealed up with phosphorus sticks in small bulbs. After sufficient time had elapsed to allow all the silver to be deposited, the bulbs were opened at varying intervals and the total phosphorus acids were determined in the solution. It will be seen that the quantity of phosphorus oxidised increases with the time, and that the values of the ratio Ag : P are much lower than those obtained before complete precipitation of the silver.

TABLE II.

Expt.	Time (days).	Ag pptd.	P oxid.	Ag : P.
1	6	0·00250	0·000717	3·49
	9		0·000807	3·10
	14		0·000865	2·89
2	7	0·00277	0·000857	3·23
	17		0·00120	2·31

The points obtained by plotting against one another the values of silver precipitated and phosphorus oxidised before complete precipitation of the silver lie approximately on a straight line which corresponds to a constant ratio of Ag : P of 4 : 1 but which does not pass through the origin. The ratio Ag : P calculated from the actual values of silver precipitated and phosphorus oxidised has, on the other hand, been shown to decrease with time. If, however, the ratio Ag : P is calculated by taking, not the values of total silver precipitated and total phosphorus oxidised from the beginning of the reaction, but the differences between subsequent values and the first value (a_0 or b_0) in each experiment, a much more constant ratio Ag : P is obtained, as shown in the last column of Table I. The average value is 4·0 : 1, if the two values shown in brackets, which are obtained from small differences, are neglected.

It would appear, therefore, that whilst at the beginning of the reaction the ratio Ag : P is higher than 4 : 1, after a certain time the main reaction taking place corresponds approximately to the precipitation of 4 atoms of silver for every atom of phosphorus oxidised.

Formation of Phosphorous Acid.—It was thought desirable to examine whether any definite relationship existed between the amounts of silver deposited and of phosphorous acid formed. Bird and Diggs supposed that the formation of phosphorous acid was due to the reduction of the phosphoric acid by the excess of

phosphorus, but this is most improbable. The further reaction between the phosphorous acid formed and the silver nitrate still in solution would, of course, introduce a complication, but experiments made to test this reaction showed that it was negligible in the concentrations used.

Phosphorus sticks were placed in solutions of silver nitrate and the amounts of phosphorous acid and of silver salt in the solution were determined at intervals. Phosphorous acid was estimated by the iodimetric method of Boyer and Bauzil (*J. Pharm. Chim.*, 1918, **18**, 321), after the excess of silver salt had been precipitated with potassium iodide. The results of several experiments are in Table III.

TABLE III.

Expt.	$AgNO_3$.	Ag pptd. ($= a$).	% of total Ag pptd.	H_3PO_3 ($= b$).	Ag : H_3PO_3 ($= a/b$).	$\frac{a-a_0}{b-b_0}$.
1	0·10	0·0704	70	0·01070	6·6	—
		0·0846	85	0·01286	6·6	6·6
		0·0975	98	0·01496	6·5	6·4
2	0·10	0·0099	9·9	0·00124	8·0	—
		0·0323	32	0·00488	6·6	6·2
		0·0420	42	0·00654	6·4	6·1
		0·0492	49	0·00770	6·4	6·1
		0·0988	99	0·01638	6·0	5·9
3	0·481	0·0695	14	0·00804	8·7	—
		0·0850	17	0·01038	8·2	6·6
		0·1240	25	0·01618	7·7	6·7
		0·425	85	0·0619	6·9	6·4
4	0·502	0·0755	15	0·00676	11·2	—
		0·0825	16·5	0·00794	10·5	5·9
		0·0910	18·4	0·00922	10·0	6·3

With $N/10$-solutions, the ratio of silver precipitated to phosphorous acid formed (Ag : H_3PO_3) is fairly constant, with the exception of one determination which was made near the beginning of the reaction. In Expts. 3 and 4, $N/2$-silver nitrate was used and determinations of the ratio Ag : H_3PO_3 were made before 25% of the total silver had been precipitated. The results are higher and not constant. If, however, the values of silver precipitated and phosphorous acid formed are plotted against one another, the points lie on straight lines having a slope corresponding to a constant ratio of Ag : H_3PO_3 of 6·3 : 1. By subtracting in each experiment the first values of silver deposited (a_0) and of phosphorous acid formed (b_0) from the subsequent values, and by using these differences to calculate the ratio Ag : H_3PO_3, fairly constant figures are obtained, as is shown in the last column of Table III.

From the quantitative experiments already mentioned, it would appear that phosphorous and phosphoric acids are produced simultaneously in constant proportion during the action of phosphorus

on silver nitrate, if we neglect the first stages of the reaction. In the following table are the results of an experiment in which the phosphorous acid and the total oxidised phosphorus ($H_3PO_3 + H_3PO_4$) were determined in a solution of silver nitrate in contact with phosphorus, at varying intervals before the silver was completely precipitated.

TABLE IV.

H_3PO_3 ($= a$).	$H_3PO_3 + H_3PO_4$ ($= b$).	a/b.	$\frac{a-a_0}{b-b_0}$.
0·00318 ($= a_0$)	0·00367 ($= b_0$)	0·87	—
0·0107	0·0156	0·69	0·63
0·0129	0·0197	0·65	0·60
0·0150	0·0236	0·63	0·59

The figures in the third column show, however, that near the beginning of the reaction phosphorous acid is the chief product formed.

Electrochemical Nature of the Reaction between Phosphorus and Metallic Salt Solutions.

Wöhler (*Annalen*, 1851, **79**, 126) found that when phosphorus was placed in a solution of copper sulphate, copper was deposited on a copper wire in contact with the phosphorus. Wicke (*ibid.*, 1852, **82**, 145) likewise noticed that silver was deposited on the surface of a silver wire in contact with phosphorus placed in silver nitrate solution; and Bird and Diggs (*loc. cit.*) described similar experiments which they regarded as evidence strongly in favour of their electrochemical theory.

Experiments were made to determine whether deposition of metal would take place on any conducting surface in contact with the phosphorus. Platinum, gold, silver, and carbon were kept in contact with phosphorus sticks immersed in solutions of silver nitrate or of copper sulphate. In every case silver or copper was deposited on the conducting surface at points far removed from the phosphorus. No metal was deposited on non-conducting surfaces in contact with the phosphorus, such as glass, or on a conducting surface which did not touch the phosphorus.

These experiments suggest that an action of an electrochemical nature is taking place and this is shown more clearly by the following experiment. A stick of phosphorus was fused on to a platinum wire and placed in a porous pot containing $N/10$-silver nitrate and standing in a beaker filled with silver nitrate of the same concentration. The free end of the platinum wire was bent over so as to make metallic connexion between the inner and outer solutions. Silver was deposited on the phosphorus and on the platinum

wire in the inner solution, and after some time the platinum wire dipping into the outer solution was covered with a bright deposit of crystalline silver. Silver was also deposited on the outer wall of the porous diaphragm at points which had apparently no metallic connexion with the platinum wire or with one another. In experiments in which no platinum wire was used, a stick of phosphorus alone being placed in the inner solution, deposition of silver again took place on the outer wall of the porous cell. This was found to be due to silver being deposited in the pores of the diaphragm, thus establishing metallic connexion between the inner and outer solutions. Deposition of silver on the outer wall of the diaphragm took place only when the inner wall was in metallic connexion with the phosphorus. Similar results were obtained by using solutions of silver sulphate or silver acetate.

In all these experiments metal ions were discharged and metal deposited—in some cases at a considerable distance from the surface of the phosphorus—only at such points as were in metallic connexion with the phosphorus surface, the contact being established either by the metal already deposited or by another conductor. The physical state of the silver and copper deposited by means of phosphorus in these experiments strongly resembled the state in which these metals are deposited from their salt solutions by an electric current. These facts favour the view that an action of an electrochemical nature takes place, *i.e.*, a direct discharge of ions to the metallic state.

Formation of a Phosphide.

The quantitative results show that owing to the formation of a phosphide in the early stages of the reaction the precipitation of the silver is not accompanied by the oxidation of an exactly equivalent amount of phosphorus. It was not found possible to ascertain the constitution of the phosphide formed, but indirect evidence indicates the probability that it is the compound Ag_3P. Moser and Brukl (*Z. anorg. Chem.*, 1922, **121**, 80) obtained this compound by the action of phosphine on silver nitrate solution and showed that it was an unstable substance capable of reacting with an excess of silver salt to give metallic silver and acids of phosphorus. The phosphide obtained by the action of phosphorus on silver nitrate was likewise decomposed by excess of silver salt. The deposit obtained by keeping a stick of phosphorus in silver nitrate solution for a short time was separated from the phosphorus, washed, and placed in $N/10$-silver nitrate. Ten c.c. of this solution, immediately after introduction of the silver deposit, were equivalent to 9·85 c.c. of a thiocyanate solution. After a few days,

10 c.c. required only 9·05 c.c. of the thiocyanate, and the solution gave a precipitate with ammonium molybdate, thus showing that silver had been precipitated and phosphorus oxidised.

The work of Christomanos (*Z. anorg. Chem.*, 1904, **41**, 309) on the action of phosphorus dissolved in ether or in benzene on solutions of copper salts pointed to the formation of a phosphide having the formula Cu_5P_2. In the case of silver salts, a black phosphide was formed, but no definite compound was isolated. Experiments were made to determine the constitution of the phosphide obtained by shaking a solution of silver nitrate with solutions of phosphorus in ether, benzene, and carbon disulphide. The black precipitate so obtained became greyer in colour after standing in contact with excess of silver salt, and it gradually assumed the appearance of metallic silver. The proportion of silver to phosphorus in the black precipitate first formed varied considerably owing to the difficulty in washing it free from excess of phosphorus without causing decomposition. The values obtained for the ratio Ag:P in the washed, but damp, precipitate varied between 2·5 : 1 and 3·9 : 1. It seems probable that, in this case also, Ag_3P is formed.

After a solution of silver nitrate had been shaken with a solution of phosphorus, the aqueous layer always contained phosphorous and phosphoric acids. The ratio of silver precipitated to phosphorus oxidised was determined. In the early stages, when the precipitate was quite black and consisted almost entirely of phosphide, high values of the order of 10 : 1 were obtained for the ratio Ag : P. When the mixture had stood for several days until the precipitate appeared to consist wholly of metallic silver, the ratio Ag : P lay between 5 : 1 and 3 : 1, *i.e.*, the values were of the same order as those obtained in the experiments with phosphorus sticks. The presence of phosphorous acid in the above experiments was due to the first reaction, *viz.*, the formation of phosphide. Silver phosphide, prepared by the action of phosphine or of solutions of phosphorus in various solvents, was washed and placed in a fresh quantity of silver nitrate solution. The phosphide was slowly oxidised to silver and phosphoric acid, no phosphorous acid being produced.

Action of Phosphorus on Solutions of Copper Salts.

The amount of phosphide formed in the case of copper salts was quite appreciable. Experiments with *N*/10-copper sulphate showed that, at the point corresponding to complete precipitation of the copper, about 13% of the total phosphorus which had reacted was present as phosphide, the remainder being in the solution as phosphorous and phosphoric acids. In the case of silver

salts, practically all the phosphorus which had reacted was present in the solution as oxy-acids.

If, however, the stick of phosphorus covered with the deposit of phosphide and copper was kept in contact with the solution for a long period, more phosphorus was oxidised, even if atmospheric oxygen was excluded, and eventually no phosphide was left in the deposit. This disposes of the suggestion of Bird and Diggs, who stated that the bright deposit of copper on remaining in contact with the phosphorus was gradually converted, as a secondary reaction, into the black phosphide. In the case of copper precipitated from a solution of the sulphate, the deposit was certainly found to turn black on standing, but it then contained no phosphorus. The deposit obtained from copper nitrate solutions retained its bright coppery colour for months. The experimental evidence shows that the phosphide formation takes place between phosphorus and metal ions, and not between phosphorus and the metal.

A determination was made of the ratio between the amounts of copper precipitated and of phosphorus oxidised before complete precipitation of the metal, the procedure being the same as in the case of silver nitrate. $N/10$- and $N/2$-Solutions of copper sulphate and copper nitrate were used. Copper was estimated in the solution volumetrically by means of thiosulphate solution. The values of copper precipitated and of phosphorus oxidised, expressed in g.-atoms per litre, are in Table V, the concentrations of copper salts being expressed in g.-mols. per litre.

TABLE V.

Expt.	Cu salt.	Time (hrs.).	Cu pptd. ($= a$).	P oxid. ($= b$).	Cu : P ($= 2a/b$).	$\frac{a-a_0}{b-b_0} \times 2$.
1	0·05	39	0·0351	0·0145	4·8	—
	$CuSO_4$	47	0·0394	0·0170	4·6	3·8
		69	0·0470	0·0209	4·5	3·8
2	0·05	39	0·0319	0·0135	4·7	—
	$Cu(NO_3)_2$.	47	0·0361	0·0156	4·6	4·1
		69	0·0445	0·0199	4·5	3·9
3	0·25	48	0·1523	0·0622	4·9	—
	$CuSO_4$	88	0·2407	0·1051	4·6	4·1
4	0·25	40	0·1437	0·0549	5·2	—
	$Cu(NO_3)_2$	88	0·2483	0·1115	4·5	3·7

The values of the ratio Cu : P have all been multiplied by 2 in order to make them comparable with the values of Ag : P. It will be seen that the value of Cu : P depends on the extent to which the reaction has proceeded. If, however, this ratio is calculated as shown in the last column, the disturbing effect of phosphide formation near the beginning is avoided and more constant values are obtained. As in the case of silver nitrate, after the reaction

between phosphorus and the metallic salt has proceeded for some time, 1 atom of phosphorus is oxidised for every 4 equivalents of the metal deposited.

Discussion and Summary.

From the experiments with silver and copper salts it appears that when a stick of phosphorus is placed in a solution of the metallic salt solution a reaction proceeds in two distinct stages. The first process is the formation of a black phosphide on the surface of the phosphorus; at the same time, the solution is found to contain phosphorous acid. After a layer of the phosphide has been formed, metal begins to be deposited in a bright crystalline state, and phosphorus is oxidised to phosphorous and phosphoric acids. During this stage, approximately 4 equivalents of the metal are deposited for every atom of phosphorus oxidised.

With regard to the formation of a phosphide, there can be little doubt that it is due to the prior production of phosphine by the action of phosphorus on water, another portion of the phosphorus being simultaneously oxidised to phosphorous acid. Strong evidence for this view is obtained from the exact parallelism which exists between the actions of phosphorus and phosphine on salt solutions of the heavy metals; only those metallic salt solutions which give phosphides by the action of phosphine are able to react with phosphorus. Cross and Higgins (J., 1879, **35**, 255) found that boiling water was decomposed by phosphorus, which was partly reduced to phosphine and partly oxidised to oxy-acids, and that, in the absence of oxygen, decomposition of the water took place only in the presence of certain metallic salts.

It is suggested, therefore, that the first stage in the action of phosphorus on the metallic salt takes place as follows (M and X representing an equivalent of the positive and negative radicals, respectively):

$$\left.\begin{aligned} 2P + 3H_2O &= PH_3 + H_3PO_3 \\ PH_3 + 3MX &= PM_3 + 3HX \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The appearance of a deposit of the metal evidently depends on the preliminary formation of the phosphide. It has already been shown that the phosphides of silver and of other metals are capable of reacting with excess of the metallic salt to give the metal and phosphoric acid. The second stage, therefore, appears to be

$$M_3P + 5MX + 4H_2O = 8M + 5HX + H_3PO_4 \quad . \quad . \quad (2)$$

According to these equations, 4 equivalents of the metal should be deposited for every atom of phosphorus oxidised, and this was the ratio actually obtained with silver and copper salts. The

amount of phosphorous acid, however, was somewhat greater than that required by these equations. It is quite possible that this may be due to the following reaction proceeding to a small extent along with reaction (2):

$$M_3P + 3MX + 3H_2O = 6M + 3HX + H_3PO_3 \quad . \quad . \quad (3)$$

As regards the phenomena which have been described as electrochemical, it must be assumed that reaction (2) is responsible for their appearance. This reaction consists essentially in the discharge of positive metal ions while phosphorus becomes oxidised, *i.e.*, loses electrons. The ionic process may be represented as $M_3P + 5M^{\cdot} = 8M + P^{\cdot\cdot\cdot\cdot\cdot}$, the positive phosphorus ions reacting immediately with water to form phosphoric acid. According to this view, the $P^{\cdot\cdot\cdot\cdot\cdot}$ ions constitute an intermediate stage in the transition from phosphide to phosphoric acid. The discharge of $M^{\cdot}$ ions and the formation of $P^{\cdot\cdot\cdot\cdot\cdot}$ ions may occur at points widely separated from one another, provided that a metallic conducting path be available for the passage of the necessary electrons.

In conclusion, I wish to thank Professor Sir James Walker, F.R.S., for his interest and helpful advice during the course of this work.

UNIVERSITY OF EDINBURGH. [*Received, March 10th*, 1926.]

CLXXVIII.—*Experiments on the Formation of Mother-of-Pearl.*

By PHANI BHUSAN GANGULY.

IT is known that mother-of-pearl, like the substance of the pearl, consists of calcium carbonate associated with water and an organic substance (conchiolin). The following is a typical analysis of mother-of-pearl (G. and H. Harley, *Proc. Roy. Soc.*, 1888, **43**, 461): Calcium carbonate, 66·0; organic matter, 2·5; water, 31·0%; total 99·5%.

As early as 1814, Brewster (*Phil. Trans.*, 1814, **104**, 397) explained the iridescent colours of mother-of-pearl as being due to two factors—a grating effect on the surface, and an interference effect caused by a thin film of calcium carbonate. The grating effect on mother-of-pearl can be easily transferred to a film of gelatin dried on its surface, and the distance between the lines can be measured. In a recent paper, Lord Rayleigh (*Proc. Roy. Soc.*, 1923, *A*, **102**, 674) has shown that the second effect is not due to a single film, but is caused by alternate layers of calcium carbonate and conchiolin, forming a series of equally spaced thin parallel plates. He ascribes the surface effect to the edges of the closely packed alternate layers

of inorganic and organic matter. This alternating structure is suggestive of the periodic precipitations which occur in the well-known Liesegang phenomenon, and as a matter of fact both Liesegang (*Kolloid Z.*, 1913, **12**, 181) and Clément and Rivière (*Compt. rend.*, 1922, **174**, 1353) have tried to produce structures similar to mother-of-pearl by the periodic precipitation of calcium phosphate in gelatin. Thus Liesegang allowed sodium phosphate to diffuse from an aqueous solution into a gelatin jelly containing calcium nitrate. The periodic structures obtained in this way exhibit some iridescence, but after a time they lose their lustre and become dull and "chalky." In order to avoid effects due to foreign electrolytes, it was decided to study the precipitation of calcium carbonate from an aqueous solution of calcium bicarbonate containing a gelatinising organic colloid.

Experimental.

The solution of calcium bicarbonate was prepared by passing carbon dioxide into a saturated solution of lime water. In this way a stock solution could be prepared at room temperature containing 0·0134 g.-mol. of calcium carbonate per litre.

With organic colloids such as gum arabic, gum tragacanth, and fish glue, no iridescent structures could be obtained by the method employed in these experiments. The best results were obtained with commercial leaf gelatin (containing 10% of moisture and 1·924% of ash). Iridescent deposits could not be obtained with a sample of highly purified and almost ash-free gelatin prepared in this laboratory. Liesegang (*Z. physikal. Chem.*, 1914, **88**, 1) has found that the best rings of silver chromate are produced when the gelatin contains small quantities of "gelatose" (a hydrolytic product of gelatin) as well as acid. All samples of commercial gelatin contain "gelatose" and therefore are most suitable for the production of Liesegang periodic layers.

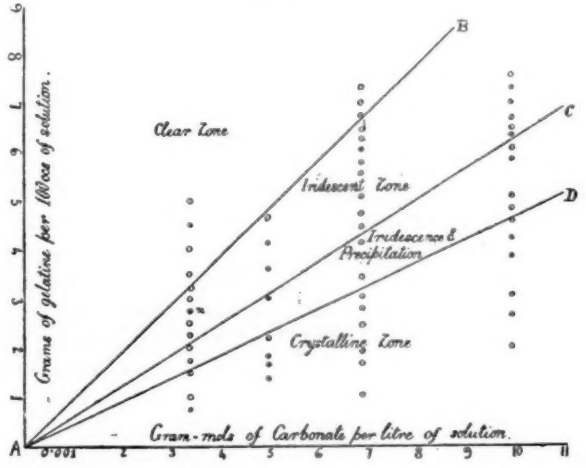
The method of procedure was as follows. Varying amounts of gelatin were weighed into a series of test-tubes, to which measured volumes of water were added. The tubes were then stoppered and the gelatin was allowed to swell, after which it was dissolved by immersing the tubes in hot water. When the solutions had cooled to about 40°, measured volumes of the calcium bicarbonate solution were run in, the contents of each tube thoroughly mixed, and drops from each placed on clean glass plates. The thin layers of gelatin–bicarbonate solution thus produced were allowed to evaporate slowly at room temperature. More rapid evaporation either at higher temperatures (*e.g.*, 50°) or in desiccators containing drying agents (or alkalis to absorb carbon dioxide) failed to give iridescent deposits of calcium carbonate. Another factor of importance in the

production of iridescence is the initial thickness of the layer of solution on the glass plate. The best results are obtained when this thickness lies between 1 and 3 mm.

An examination of the dried layers showed that for a given initial concentration of calcium carbonate the result depended on the concentration of gelatin. With any given initial calcium carbonate concentration and increasing gelatin concentrations, four types of product, corresponding to four fairly well demarcated regions, were in general obtained :

Region 1.—If the gelatin concentration lies below a certain value, there is produced an irregular crystalline deposit, with a thicker aggregation of calcium carbonate crystals at the centre, but no iridescence.

FIG. 1.



Region 2.—If the gelatin concentration is somewhat higher, iridescent specks appear, generally in the centre, together with a visible deposit of calcium carbonate crystals all over the area. In this case the calcium carbonate usually formed a series of coarse irregular rings.

Region 3.—With a still higher gelatin concentration there is no visible deposit of calcium carbonate, and the whole area, now quite translucent, shows a beautiful mother-of-pearl-like iridescent colour, varying with the angle of observation.

Region 4.—Finally, if the gelatin concentration exceeds a certain value, the layer remains clear and translucent, but exhibits no colour.

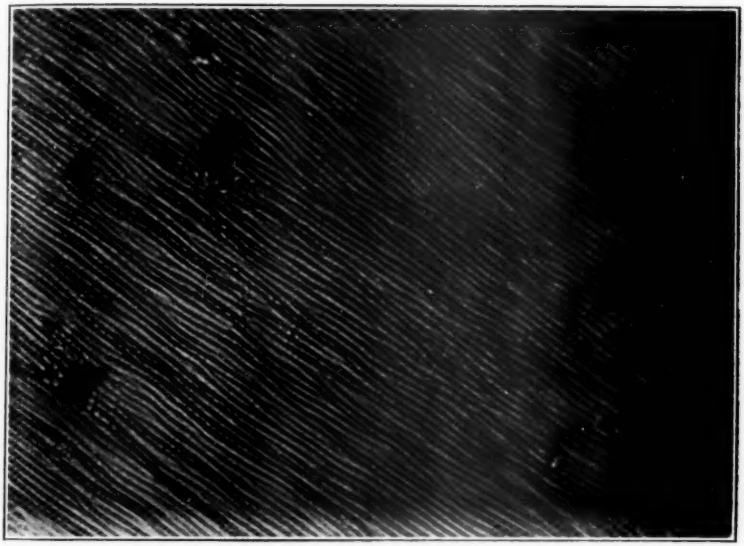
The general nature of the results obtained is well shown in the accompanying figure. The lines AB, AC, AD, together with the axes, divide the diagram into the four regions or zones already

described, although it must be understood that the positions of these lines are not fixed with any great degree of precision.

Microscopic examination of the thin iridescent plates of gelatin–calcium carbonate corresponding to the zone AB—AC shows that the slowly decomposing calcium bicarbonate has deposited the calcium carbonate in a series of more or less regular and parallel layers or sheets resembling those of a Liesegang structure. Various photomicrographs were taken and the spacing of the layers was determined by means of a Hilger travelling microscope. There were present 4000—6000 layers per cm. The accompanying photograph shows the type of structure obtained.

Discussion of Results.

These experiments show that it is possible to prepare a clear, translucent, thin plate or sheet of dried gelatin containing a very fine spatially periodic precipitation of calcium carbonate and exhibiting the iridescent colour effects characteristic of mother-of-pearl. The colours shown by the preparations described in this paper are in all probability due to a grating effect caused by the closely-spaced layers of calcium carbonate, although it has not been found possible to determine by means of sections the exact orientation of these layers with respect to the surface of the thin plate of gelatin. Nevertheless, the photomicrographs show clearly enough that the layers of calcium carbonate do not lie parallel to the surface of the gelatin plane, but must be oriented at an angle to it which probably does not differ much from 90°. Each drop of solution produces a thin, more or less circular, lens-shaped disc on the glass plate. It is probable that the precipitation of calcium carbonate begins at the surface of the outer rim, and proceeds rhythmically in a series of closely-spaced concentric rings towards the central part of the surface of the evaporating disc of solution. As evaporation of water and carbon dioxide proceeds, this rhythmic precipitation is carried more or less vertically downwards, *i.e.*, at right angles to the main surface of the disc. The result of such a periodic precipitation would be to yield a grating surface capable of producing colours in reflected light, provided the spacing be fine enough. Although this is the most probable explanation of the colour effects described in this paper, the possibility of colour production by interference of light reflected from a series of parallel plates cannot be excluded. Taken in conjunction with the work of Brewster and of Lord Rayleigh, the synthetic chemical experiments described leave little doubt as to the origin of the colours exhibited by mother-of-pearl. The thin sheets of gelatin–calcium carbonate which have been obtained approach very closely in their nature and structure



Microphotograph of gelatin-calcium carbonate. ×560.
(*Corresponding to* x *in the figure.*)

[*To face p.* 1384.]

to natural mother-of-pearl, and may indeed be described as " elements " of mother-of-pearl, although, of course, the organic colloid used is different from the " conchiolin " of the natural material.

Summary.

1. The deposition of calcium carbonate from a thin layer of an aqueous solution of calcium bicarbonate in the presence of gelatin has been studied.
2. The nature of the deposit depends upon the initial concentration of calcium bicarbonate and the ratio of gelatin to calcium bicarbonate.
3. For any given initial concentration of calcium bicarbonate there is a range of gelatin concentrations which yield translucent layers showing the iridescent colours characteristic of mother-of-pearl.
4. The structure of mother-of-pearl has been discussed in the light of these experiments and the physical work of Brewster and of Lord Rayleigh.

In conclusion, the author wishes to express his thanks to Professor Donnan for suggesting this problem to him and for his kind interest and guidance in the work.

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CLXXIX.—*Aminobenzthiazoles. Part III. The Tautomerism and Unsaturation of the Aminothiazole System.*

By ROBERT FERGUS HUNTER.

As one of the three objects * of this investigation (see Part I, J., 1925, **127**, 2023), the mobility of the symmetrical triad system

$$[H]\cdot N\cdot C{:}N \rightleftharpoons N{:}C\cdot N[H]$$

* A fourth object, *viz.*, the study of the relation between unsaturation and mobility in tautomeric triad systems of the aminothiazole type, is of particular interest in connexion with the whole philosophical aspect of tautomerism involving a mobile hydrogen atom (compare Thorpe, J., 1923, **123**, 1361; Kon, Stevenson, and Thorpe, J., 1922, **121**, 650), and will be fully dealt with in a later paper. In the 5-bromo-1-alkylaminobenzthiazoles, the increasing molecular volume of the alkyl group in the ethyl, *n*-propyl, *n*-butyl, *iso*butyl series tends to enhance the aminothiazole phase of the system, and consequently to increase the stability of the dibromo-addition compounds. Indeed, in the ethyl series Mr. Soyka and myself were able

in 1-amino- and substituted 1-aminobenzthiazoles has been examined, with the result that the tautomerism of the 1-aminobenzthiazole system (I) with the corresponding 1-imino-1 : 2-dihydrobenzthiazole complex (II) has been established.

(I.) $C_6H_4\langle{}^{S-}_{N}\rangle C\cdot NH_2 \rightleftharpoons C_6H_4\langle{}^{S}_{NH}\rangle C{:}NH$ (II.)

There are three tests for the mobility of symmetrical triad systems (Ingold and Piggott, J., 1922, **121**, 2381; 1923, **123**, 1470): (A) The symmetry test, (B) the fission test, and (C) the substitution test (compare also Farrow and Ingold, J., 1924, **125**, 2543). Only the first and third of these tests are applicable to the system under discussion. There exists already in the literature of 1-aminobenzthiazole evidence of the symmetry type. Thus, whilst the classical synthesis of this compound from 1-chlorobenzthiazole (Hofmann, *Ber.*, 1879, **12**, 1126) is usually regarded as a proof of the constitution (I), its synthesis from phenylthiosemicarbazide (Fischer and Besthorn, *Annalen*, 1882, **212**, 326) * can be formulated only in terms of the iminodihydro-structure (II).

The symmetry test, however, was more definitely established by the synthesis of 1-acetylaminobenzthiazole (VII) and 1-*imino*-2-*acetyl*-1 : 2-*dihydrobenzthiazole* (VIII) from the *bromides* (V) and (VI), respectively, which were obtained by bromination of the stable and labile forms of acetylphenylthiocarbamide (Hugershoff, *Ber.*, 1899, **32**, 3649; Wheeler, *Amer. Chem. J.*, 1902, **27**, 270; Hunter, *loc. cit.*). On hydrolysis, the two isomeric acetyl derivatives

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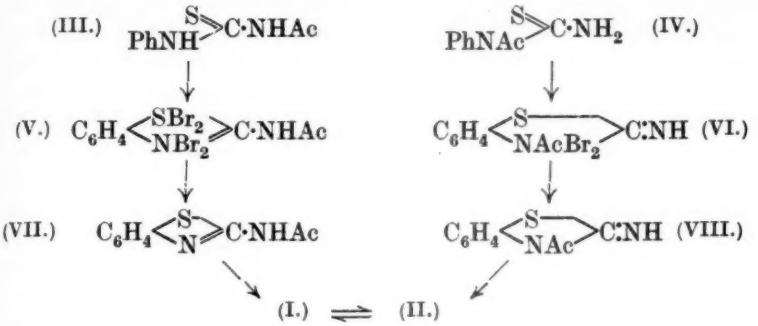
to isolate both forms of the dibromide, which must be regarded as being of the type $[H]NBr_2{\cdot}C{:}NEt$ and $NBr_2{:}C{\cdot}N[H]Et$, respectively. These forms were strikingly different in physical properties and in their reducibility by hydriodic acid (compare West, J., 1924, **125**, 710 and other papers). Both gave the same ethylamino-base on reduction with sulphurous acid and, moreover, the labile form was converted into the more stable form by boiling for some time with a mixture of bromine and chloroform. This conversion shows that it is at least probable that at some stage an equilibrium $[H]NBr_2{\cdot}C{:}NEt \rightleftharpoons NBr_2{:}C{\cdot}N[H]Et$, which is apparently a case of retarded mobility (Kon and Linstead, J., 1925, **127**, 815) involving quinquevalent nitrogen, may occur. In view of this, it has seemed desirable to institute a series of experiments on the bromination both of mobile and of "nascently" mobile (compare Goss and Ingold, J., 1925, **127**, 2776) systems of the amidine type.

In the bromination of *s*-di-β-naphthylthiocarbamide in chloroform (J., 1925, **127**, 2270) two forms of the hexabromide of 2-β-naphthylamino-α-naphthathiazole were accidentally isolated, and only one of these was obtained by bromination of the naphthathiazole base itself.

* Fischer and Besthorn's "phenylthiocarbazine," obtained by the action of 20% hydrochloric acid on phenylthiosemicarbazide at 125—130°, was shown by Hugershoff (*Ber.*, 1903, **36**, 3134) to be 1-aminobenzthiazole.

(VII and VIII) yielded the same 1-aminobenzthiazole (or 1-imino-1 : 2-dihydrobenzthiazole).



With regard to the third test (C), it was found that 1-aminobenzthiazole methylates almost exclusively in the imino-form (II), yielding 1-*imino*-2-*methyl*-1 : 2-*dihydrobenzthiazole* (XI), whose constitution was established by rational synthesis from *as*-methylphenylthiocarbamide (IX) by way of the *dibromide* (X). During the methylation a more soluble isomeride was also produced. This, owing to experimental difficulties, could not be obtained pure, but it was undoubtedly 1-*methylaminobenzthiazole* (XIV), which was also synthesised from *s*-methylphenylthiocarbamide (XII) by way of the *tetrabromide* (XIII). [Formulæ IX, X, and XI are IV, VI, and VIII, respectively, and XII, XIII, and XIV are III, V, and VII, respectively, all with Me in place of Ac.]

The ethylation of 1-aminobenzthiazole proved more troublesome than the methylation. The bulk of the product was, however, finally identified as 1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole*, whose constitution was established by its synthesis from *as*-ethylphenylthiocarbamide by way of the *tetrabromo*-addition compound as in the case of the corresponding methyl derivative.

The acetylation of 1-aminobenzthiazole was studied in the hope of isolating both acetyl derivatives (VII and VIII). The base acetylated almost completely in the amino-form (I), giving 1-acetylaminobenzthiazole, and although on several occasions the presence of a small amount of a low-melting acetyl derivative was observed, the second isomeride could not be isolated pure.

The substitution test (C), therefore, supports the symmetry test (A), since with a reagent favouring the imino-form, the triad system reacts almost completely in this form, the methyl group attaching itself almost exclusively to the less basic nitrogen atom (Marckwald, *Annalen*, 1895, **286**, 343; von Pechmann, *Ber.*, 1895, **28**, 869, 2362; 1897, **30**, 1779; Cohen and Marshall, J., 1910, **97**, 328), whilst with

acetic anhydride, which favours the amino-form, the amidine system reacts almost completely in the latter form, yielding the 1-acetylamino-derivative.

Although experimental difficulties prevented the isolation in a pure condition of two methyl or ethyl derivatives, there can be no doubt that in both cases both alkyl derivatives were actually present, for Pyman has shown (J., 1923, **121**, 367, 3359) that, on alkylation, an amidine whose two nitrogen atoms differ in basicity invariably yields two alkyl derivatives, a very small quantity of the isomeride corresponding to the more basic form of the amidine accompanying a large quantity of the more readily formed alkyl derivative. The two nitrogen atoms in the aminothiazole system differ considerably in basicity, this being shown by the base acetylating almost completely in the more basic form.

Mobility in 1-aminobenzthiazole having thus been established, the general chemistry of the substance was studied. The base was readily converted into an unstable diazonium chloride, which coupled with β-naphthol in the usual way. Attempts to convert the diazonium chloride into 1-hydroxybenzthiazole, however, invariably yielded 1-*aminoazobenzthiazole hydrochloride*,

$$C_6H_4\langle\overset{S}{N}\rangle C\cdot N_2\cdot C_6H_3\langle\overset{S}{N}\rangle C\cdot NH_2,HCl$$

(compare Hantzsch and Popp, *Annalen*, 1889, **250**, 257).

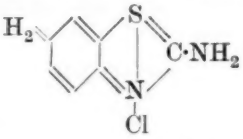
The aminothiazole appeared to react in the normal way with formaldehyde and acetaldehyde, but pure condensation products could not be isolated. Attempts to condense the base with benzaldehyde failed. This is readily understood, however, since the formation of the benzylidene derivative would involve the removal of both the mobile hydrogen atom and the potentially mobile hydrogen atom of the triad system.

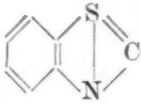
The base benzoylated normally, giving 1-*benzoylaminobenzthiazole*, which on treatment with an excess of bromine yielded a *tetrabromide* (formula as V). Under the influence of dilute alcohol this yielded 5-*bromo*-1-*benzoylaminobenzthiazole*. The fact that the presence of a benzoyl group only allows the formation of a tetrabromide in circumstances in which 1-acetylaminobenzthiazole readily passes into a *hexabromide* is probably to be attributed to the steric effect of the phenyl group in the benzoylamino-residue.

1-Aminobenzthiazole reacts very readily with sodium hypochlorite, yielding a deep purple dye of the rosaniline type.

On treating 1-aminobenzthiazole hydrochloride with alcoholic ethyl nitrite, neither the expected 1-imino-2-nitroso-1 : 2-dihydrobenzthiazole nor benzthiazole itself was produced, but the *hydrochloride* of a new base, isomeric with 1-aminobenzthiazole, which

crystallised in beautiful ruby-red prisms. The *base* itself was very pale yellow. A similar reaction was observed in the cases of 1-amino-3-methyl- and 1-amino-5-methyl-benzthiazole. Possibly the intensely coloured hydrochloride and the base may have formulæ (XV) and (XVI)), respectively (compare Kehrmann, *Ber.*, 1906, **39**, 914; Smiles and Hilditch, J., 1908, **93**, 145, 1687; Battegay and Vechot, *Bull. Soc. chim.*, 1925, **37**, 1271).

XV.) 

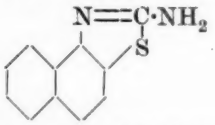
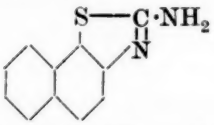
 (XVI.)

The tautomerism of 5-bromo-1-aminobenzthiazole and 5-bromo-1 imino-1 : 2-dihydrobenzthiazole was established by means of the symmetry test (A). The hexabromide of 1-acetylaminobenzthiazole, $C_6H_4<\begin{matrix}SBr_4^-\\NBr_2\end{matrix}>C{\cdot}NHAc$, was converted into 5-*bromo*-1-*acetyl-aminobenzthiazole*, and the dibromide of 1-imino-2-acetyl-1 : 2-dihydrobenzthiazole (VI) into the isomeric 5-*bromo*-1-*imino*-2-*acetyl*-1 : 2-*dihydrobenzthiazole*, by treatment with dilute alcohol (compare Hunter, J., 1925, **127**, 2026). On hydrolysis both these 5-bromo-acetyl derivatives yielded the same 5-bromo-1-aminobenzthiazole (formula as I or II). The fission test (B) is inapplicable in this case, and the substitution test (C) was not investigated in view of the difficulties encountered in the previous case.

In view of the curious observations made regarding the bromides of the *o*-, *m*-, and *p*-toluidinomethylbenzthiazoles (*loc. cit.*), the bromo-addition compounds of 1-amino-3-methyl-, 1-amino-4-methyl- and 1-amino-5-methyl-benzthiazole were examined. Whereas *o*-tolylthiocarbamide readily passed into the *dibromide* of the first, *m*-tolylthiocarbamide gave the labile *tetrabromide* of the second, $C_6H_3Me<\begin{matrix}SBr_2^-\\NBr_2\end{matrix}>C{\cdot}NH_2$, whilst *p*-tolylthiocarbamide yielded a more stable *tribromo*-addition compound of the last, which is doubtless the hydrobromide of the dibromide. This tribromide was on one occasion isolated in two forms (compare the case of 2-β-naphthylamino-α-naphthathiazole hexabromide, J., 1925, **127**, 2274).

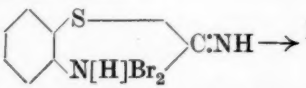
Bromination of *m*-xylylthiocarbamide gave the *tetrabromide* of 1-amino-3 : 5-dimethylbenzthiazole, which is the most labile amino-thiazole bromide so far isolated. The instability is clearly to be attributed to the methyl groups in positions 3 and 5, there being no possibility either of *o*- or of *p*-migration of bromine into the aromatic nucleus (compare Fries, *Annalen*, 1906, **346**, 128).

Lastly, the bromides of 2-amino-β-naphthathiazole (XVII) and 2-amino-α-naphthathiazole (XVIII) were examined. Both α- and β-naphthylthiocarbamide on bromination readily yielded the *tetrabromides* of (XVII) and (XVIII), respectively. These are compounds of the usual type, but are more stable than the bromides of the aminobenzthiazole series, no doubt owing to the presence of the naphthalene nucleus, since the bromo-addition compounds of 2-β-naphthylamino-α-naphthathiazole (*loc. cit.*) are remarkably stable under ordinary laboratory conditions.

(XVII.)   (XVIII.)

1-Imino-2-methyl-1 : 2-dihydrobenzthiazole (XI) on bromination yielded a stable orange-yellow *tribromide* of the type obtained by exposing the higher bromides of the 1-tolylaminodimethylbenzthiazole series (*loc. cit.*) to moist air.

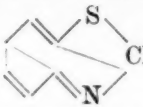
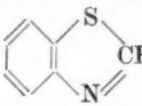
The dibromide of 1-aminobenzthiazole (XIX) (Hugershoff, *Ber.*, 1901, **34**, 3130; 1903, **36**, 3121) obtained by brominating phenylthiocarbamide in chloroform, on treatment with warm water, is instantly converted into 5-bromo-1-imino-1 : 2-dihydrobenzthiazole hydrobromide (XX).

(XIX.)  (XX.)

This transformation is clearly a para-migration, analogous in some respects to the *N*-bromoacetanilide → *p*-bromoacetanilide isomerisation (Chattaway and Orton, J., 1899, **75**, 1046; 1900, **77**, 134, 152, 789, 797), but differing from it in that the nitrogen atom is in the quinquevalent state. The passage of the dibromide into the bromo-hydrobromide can be explained by means of a bridged form of the benzthiazole nucleus (XXI) (compare Ingold, J., 1922, **121**, 1133, 1143) analogous to the formula which Shearer (*Proc. Phys. Soc.*, 1923, **35**, ii, 81) has assigned to naphthalene on the basis of *X*-ray analysis.*

* The parachors (J., 1925, **127**, 1525 and later papers) of 1-aminobenzthiazole and of certain other benzthiazole derivatives are being determined by Dr. Sugden in the hope that they may give some indication of the intra-annular exchanges which take place in the benzthiazole system. Unfortunately, the difference between the calculated values of the parachor for the ordinary form of 1-aminobenzthiazole (I or II) ([P] = 311·9) and for the bridged form suggested in this paper as a phase of the benzthiazole system ([P] = 308·9) is very small (Sugden, private communication) and may not be capable of definite experimental detection.

The bridged formula (XXI) represents only *one* of the intra-annular phases of benzthiazole, in tautomeric equilibrium with the

(XXI.)  ⇌  (XXII.)

normal phase (XXII), which is the usually accepted structure for the substance. The bridged form involves a hypothetical form of the thiazole nucleus, analogous to the bridged formula of thiophen (Farmer, Ingold, and Thorpe, J., 1922, **121**, 134) and the intra-annular five-carbon nucleus (*idem*, *loc. cit.*; Ingold, Seeley, and Thorpe, J., 1923, **123**, 863; Grimwood, Ingold, and Thorpe, *ibid.*, p. 3303). The strikingly aromatic properties of the thiazole nucleus (Hantzsch and collaborators, *loc. cit.*) suggest that the thiazole ring must, if the views of Ingold and his collaborators (J., 1922, **121**, 1133, 1143; 1923, **123**, 2066, 2081) regarding aromatic nuclei are correct, be a tautomeric system, although in view of the difficulties which heterocyclic nuclei present in this connexion from the experimental point of view (Ingold and Piggott, J., 1922, **121**, 2749; Ingold, J., 1924, **125**, 87), the problem of obtaining direct evidence of a bridged form of the thiazole nucleus appears at the present time to be insoluble. Evidence of a bridged form of the benzthiazole system must, however, be taken as *indirect* evidence on this point, and a series of experiments has been instituted in the hope of proving that the bridged formula (XXI) represents *one* phase of the benzthiazole system. With regard to the 1-amino-benzthiazole dibromide → 5-bromo-1-imino-1 : 2-dihydrobenzthiazole hydrobromide change, it is suggested, not that this transformation is a proof of the bridged structure of the benzthiazole nucleus, but merely that it is best explained on the basis of the latter. The exceedingly beautiful fluorescence of certain benzthiazole derivatives (Hunter, *Chemical News*, 1923, **127**, 385) is noteworthy in connexion with the problem of the bridged phase (compare Kaufmann, *Ahrens Vorträge*, 1908, **12**, 35; Ingold, J., 1922, **121**, 1134).

Experimental.

(Substances exhibiting amino–iminodihydro-tautomerism are named on the basis of their amino-formula).

The Mobility of 1-*Aminobenzthiazole.*

Methylation.—1-Aminobenzthiazole (2 g.) was heated with methyl iodide (1·6 c.c.) at 100° for 5 hours. The product, after being treated with alkali and with hot water to remove any unchanged amino-base, crystallised from alcohol in plates, m. p. 115°. After

recrystallisation from benzene it melted at 122° and did not depress the m. p. of an authentic specimen of 1-imino-2-methyl-1 : 2-dihydrobenzthiazole (XI). It was further characterised by the formation of the stable, yellow-orange tribromo-addition compound (page 1393).

In an experiment similar to the above, the methylation product was extracted with cold ether and alcohol. The extract on evaporation yielded a clear pale yellow gum, which could not be crystallised, consisting of the more soluble methyl derivative. After the gum had solidified, it melted at about 114°. Mixed with a specimen of 1-methylaminobenzthiazole, it melted at 120° after softening at about 100°.

Ethylation.—1-Aminobenzthiazole (2 g.) and ethyl iodide (1·5 c.c.) were heated at 100° for 5—6 hours. The product, after treatment with alkali and warm water, was usually obtained as a tenacious gum, which sometimes solidified on standing for some weeks. On trituration with ether the product sometimes crystallised. It had m. p. 85° and was identified as 1-imino-2-ethyl-1 : 2-dihydrobenzthiazole (mixed melting point determination).

Acetylation.—A solution of 8 g. of 1-aminobenzthiazole in acetic anhydride (30 c.c.) was heated under reflux and cooled and the crystalline acetyl derivative was collected. The filtrate was mixed with alcohol and evaporated; small needles, m. p. 115°, were thus obtained. The acetyl derivative (7 g.) was extracted with boiling alcohol; the residue of small prisms had the same m. p., 186°, as the lustrous plates of 1-acetylaminobenzthiazole deposited from the extract. The remaining liquors were fractionally crystallised, but although low-melting substances (m. p. 120°) were frequently obtained, 1-imino-2-acetyl-1 : 2-dihydrobenzthiazole could not be isolated pure. The yield of pure 1-acetylaminobenzthiazole was almost quantitative. The crude acetylation product had no action on sodium hypobromite, showing the absence of unchanged base.

1-*Imino*-2-*methyl*-1 : 2-*dihydrobenzthiazole Dibromide* (X).—*as*-Methylphenylthiocarbamide (1 g.) in chloroform (10 c.c.) was gradually treated with a solution of bromine (0·8 c.c.) in chloroform (3 c.c.); a bulky orange precipitate separated which redissolved with evolution of heat and hydrogen bromide. The mixture was refluxed for 2 minutes and cooled; the bulk of the product then separated in tile-red crystals. The filtrate gradually deposited the *dibromide* in glistening, orange-red needles which, after drying in a vacuum over potassium hydroxide, sintered and softened at 125° (Found : Br, 49·8. $C_8H_8N_2Br_2S$ requires Br, 49·4%). The dibromide had the usual properties of these compounds, and slowly became yellow in the air with loss of bromine.

1-*Imino*-2-*methyl*-1 : 2-*dihydrobenzthiazole* (XI).—The dibromide, suspended in sulphurous acid, was treated with sulphur dioxide until a colourless solution was obtained. This, on being made alkaline with ammonia, deposited the free methyl base in small prisms, m. p. 123° (Found : S, 18·9. $C_8H_8N_2S$ requires S, 19·5%).

1-*Imino*-2-*methyl*-1 : 2-*dihydrobenzthiazole Tribromide*.—The methyl derivative (0·2 g.) dissolved in chloroform (7 c.c.) was slowly treated with an excess of a 20% solution of bromine in the same solvent; an orange precipitate of the bromo-addition compound was obtained. The mixture was warmed and then cooled in ice. The *tribromide*, after being dried in a vacuum, was obtained in minute, orange prisms which lightened at 230—240° and became white without melting at 245° [Found : Br, 59·8. $(C_8H_8N_2Br_3S)_2$ requires Br, 59·4%].

1-*Methylaminobenzthiazole Tetrabromide* (XIII).—A solution of *s*-methylphenylthiocarbamide (4 g.) in chloroform (25 c.c.) was gradually treated with bromine (3·2 c.c.) and heated under reflux for a few minutes. On cooling, the *tetrabromide* crystallised in rosettes of shining, scarlet needles, m. p. 65—67° (decomp.), which were dried in a vacuum over potassium hydroxide (Found : Br, 66·1. $C_8H_8N_2Br_4S$ requires Br, 66·1%).

The tetrabromide was exposed to the air for 20 hours (compare 1-anilinobenzthiazole tetrabromide ⟶ tribromide transformation; J., 1925, **127**, 2026), losing bromine with the formation of a yellow-orange *dibromide*. This was extracted with chloroform, and separated on scratching in small, orange-yellow prisms which, after drying in a vacuum, sintered at 136° and charred at 191° (Found : Br, 48·8. $C_8H_8N_2Br_2S$ requires Br, 49·4%). The dibromide, however, differed from the tribromides of the 1-arylaminobenzthiazoles (*loc. cit.*) in losing more bromine on prolonged exposure to air.

Bromo-substitution Derivatives.—The tetrabromide dissolved readily in hot absolute alcohol, and on diluting the solution with water and concentrating it, a crystalline mass of the hydrobromides of the bromo-substitution products was obtained. This was treated with ammonia and the liberated bases were crystallised from ethyl acetate–alcohol, from which silky, lustrous plates of a mixture of monobromo- and dibromo-substitution derivatives were obtained, m. p. 203°; these could not be separated (Found : Br, 46·8. $C_8H_7N_2BrS$ requires Br, 37·0%. $C_8H_6N_2Br_2S$ requires Br, 49·9%). This behaviour is curious, for in all previous experiments on the bromination of substituted benzthiazoles it was possible to introduce only one bromine atom into the benzene nucleus (Hunter, this vol., p. 540).

1-*Methylaminobenzthiazole* (XIV).—The tetrabromide was suspended in sulphurous acid and treated with sulphur dioxide. The crystalline paste of salts obtained was slowly added to a strong solution of ammonia, in which it dissolved. The base crystallised on cooling, and a further small quantity was obtained by extracting the filtrate with ether. The base was obtained from dilute alcohol in tufts of silky needles, m. p. 135°, and finally from absolute alcohol in prisms, m. p. 138° (Found: S, 19·8. $C_8H_8N_2S$ requires S, 19·5%).

1-*Imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole tetrabromide* was obtained from *as*-ethylphenylthiocarbamide (3 g.) and bromine (2·2 c.c.) in chloroform by the method for preparing the dibromide (X). After drying in a vacuum over potassium hydroxide, the tetrabromide was obtained in glistening, vermilion-orange prisms, m. p. 160—161° (decomp., with previous sintering) (Found: Br, 62·6. $C_9H_{10}N_2Br_4S$ requires Br, 64·3%).

1-*Imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole*, prepared by reducing the preceding tetrabromide (10 g.) in the usual way, was obtained as a gum which solidified; it crystallised from alcohol in pale yellow prisms, m. p. 86° (Found: S, 18·1. $C_9H_{10}N_2S$ requires S, 17·9%).

Labile Acetylphenylthiocarbamide.—Phenylthiocarbamide (16 g.) was heated with acetic anhydride (14 c.c.) at 80° (Hugershoff, *loc. cit.*). The product crystallised from ethyl acetate in prisms, m. p. 136°; after recrystallisation it melted at 138°.

1-*Imino*-2-*acetyl*-1 : 2-*dihydrobenzthiazole Dibromide* (VI).—(A) The labile acetylphenylthiocarbamide (2 g.) dissolved in chloroform (25 c.c.) was gradually treated with bromine (1·2 c.c.). Heat and hydrogen bromide were evolved in the usual way and crystallisation took place in the hot solution towards the end of the bromination. The mixture was refluxed for a short time, cooled, and the *dibromide* collected and dried in a vacuum; it was then obtained in glistening orange prisms, m. p. 130—132° (decomp.) (Found: Br, 45·6. $C_9H_8ON_2Br_2S$ requires Br, 45·5%).

(B) The acetylphenylthiocarbamide (2 g.) dissolved in 12 c.c. of chloroform was gradually treated with 1·6 c.c. of bromine; hydrogen bromide was evolved and a dark red tar produced. The solvent was decanted off and the tar boiled for 1 minute with 20 c.c. of absolute alcohol, being thereby changed into fine purplish-red prisms, which were dried in a vacuum. This *dibromide* sintered at about 160° and melted at 173° (decomp.) (Found: Br, 42·3%).

This dibromide showed the most striking stability to air, and appreciably lost bromine only over a period of some weeks. It was also more slowly reduced by sulphurous acid than the other bromides of 1-imino-2-acetyl-1 : 2-dihydrobenzthiazole.

1-*Imino*-2-*acetyl*-1 : 2-*dihydrobenzthiazole Dibromide Hydrobromide*.—The labile acetylphenylthiocarbamide (4 g.) dissolved in chloroform (30 c.c.) was gradually treated with bromine (3 c.c.), and the mixture boiled. The product consisted of small, shining, dark chocolate-coloured prisms which were dried in the usual way. They became suddenly orange at 178° and melted at 180° (decomp.) (Found: Br, 55·6. $C_9H_8ON_2Br_2S,HBr$ requires Br, 55·7%). This bromide had the usual properties, being reduced by sulphurous acid and converted into the substitution derivative by treatment with diluted alcohol, and was strikingly similar to the dibromide of 4′-amino-1-phenyl-5-methylbenzthiazole (J., 1925, **127**, 1318) in appearance and stability in air.

1-*Imino*-2-*acetyl*-1 : 2-*dihydrobenzthiazole* (VIII).—This was obtained from the dibromide by means of sulphurous acid and ammonia in the usual way. It separated from 20% alcohol in minute crystals, m. p. 118—120° (Found: S, 17·2. $C_9H_8ON_2S$ requires S, 16·7%).

Hydrolysis. A part of the product was hydrolysed with 60% sulphuric acid, the solution neutralised at 0°, and the product recrystallised from hot water. Lustrous plates of 1-aminobenzthiazole were thus obtained which, alone or mixed with a genuine specimen, melted at 126°. The base was further characterised by the formation of the dibromide and of benzthiazole-1-azo-β-naphthol.

Specimens of the acetyl derivative have sometimes been obtained from alcohol–ethyl acetate in pale yellow prisms, m. p. 140° (or higher); these also yield 1-aminobenzthiazole on hydrolysis with 60% sulphuric acid, but have not yet been fully investigated.

Stable Acetylphenylthiocarbamide.—The labile acetyl derivative (18 g.) was kept at 150—160° for 10 minutes and then at 170—180° for an equal time. The product crystallised from alcohol–ethyl acetate in prisms, m. p. 170—171°, as recorded (*loc. cit.*).

1-*Acetylaminobenzthiazole Tetrabromide* (V).—When stable acetylphenylthiocarbamide (1 g.) in chloroform (7 c.c.) was slowly treated with bromine (0·9 c.c.), hydrogen bromide was evolved and a clear red gum separated. The mixture was boiled and cooled. On being rubbed, the gum solidified to a mass of orange-red prisms which were dried in the usual way; m. p. 137—139° (Found: Br, 61·8. $C_9H_8ON_2Br_4S$ requires Br, 62·5%).

1-*Acetylaminobenzthiazole* (VII) was obtained from the tetrabromide (1 g.) in the usual way. It crystallised from alcohol in prisms, m. p. 186°, and was identical with the acetyl derivative obtained by the direct acetylation of 1-aminobenzthiazole.

1-*Benzoylaminobenzthiazole*, obtained from 1-aminobenzthiazole

(1 g.) by the Schotten-Baumann method, crystallised from alcohol in prisms, m. p. 186° (Hugershoff, *loc. cit.*).

1-*Benzoylaminobenzthiazole Tetrabromide.*—The benzoyl derivative (0·4 g.) dissolved in 5 c.c. of chloroform was treated with bromine (0·3 c.c.), and the solution boiled. On cooling, the *tetrabromide* crystallised in silky, orange-yellow plates which, after drying in a vacuum, lightened in colour at about 170° and became colourless and lost bromine at about 185° (Found: Br, 56·8. $C_{14}H_{10}ON_2Br_4S$ requires Br, 55·8%).

5-*Bromo*-1-*benzoylaminobenzthiazole.*—A solution of the tetrabromide in alcohol was boiled, diluted, and evaporated, the white, crystalline product was treated with ammonia, and the *bromo*-derivative was dried and recrystallised from ethyl acetate, separating in small prisms, m. p. 226° (Found: Br, 25·2. $C_{14}H_9ON_2BrS$ requires Br, 24·0%).

Benzthiazole-1-*azo*-β-*naphthol.*—A solution of aminobenzthiazole (1·5 g.) in 20 c.c. of dilute hydrochloric acid was diazotised in the usual way, and the product coupled with 1·4 g. of β-naphthol dissolved in 8 c.c. of 5% sodium hydroxide solution. The orange-brown azo-compound was collected and extracted with ether; the extract, on evaporation in a vacuum at room temperature, left the azo-compound in deep purple-red prisms, m. p. 146° after sintering at 140° (Found: S, 10·3. $C_{17}H_{11}ON_3S$ requires S, 10·5%). The product dyed cotton a fugitive shade of yellow. On reduction with tin and hydrochloric acid it gave 1-aminobenzthiazole, which was identified by its m. p. and by the m. p. of its mixture with a genuine specimen.

1-*Aminoazobenzthiazole.*—A solution of diazotised 1-aminobenzthiazole (prepared from 4 g. of the base in 50 c.c. of water and 10 c.c. of concentrated hydrochloric acid) was boiled for an hour, filtered from tar [which did not yield any trace of 1-hydroxybenzthiazole (Jacobson, *Ber.*, 1886, **19**, 1811) on extraction with alkali] and concentrated. The red crystals of the *hydrochloride* obtained separated from alcohol (animal charcoal) in yellow prisms, m. p. 232° (decomp.) after softening at 224°. The *base* was obtained by treating it with ammonia and was crystallised from ether and from boiling water, separating in small, cream-white, lustrous plates, m. p. 135° (Found: S, 21·6. $C_{14}H_9N_5S_2$ requires S, 20·7%). On reduction with tin and hydrochloric acid, 1-aminobenzthiazole was isolated and identified (m. p. and mixed m. p. determination).

Reaction of 1-*Aminobenzthiazole with Sodium Hypochlorite.*—The base (1 g.) in 30 c.c. of water was gradually treated with 50 c.c. of 0·3*N*-sodium hypochlorite. The purple precipitate produced, after being washed with a little ether, separated from chloroform–

light petroleum at 20° in dark purple crystals, which softened at 156—158°. The compound had dyeing properties of the usual type.

ψ-Aminobenzthiazole Hydrochloride (XV).—The hydrochloride from 5 g. of 1-aminobenzthiazole was suspended in 80 c.c. of alcohol at 5° and slowly treated with 16·5 c.c. of a 15% alcoholic solution of ethyl nitrite. The mixture became yellow on addition to 50 c.c. of boiling alcohol and thereafter bright orange on refluxing for a short time. On spontaneous evaporation, clusters of hard, shining, ruby-red prisms were obtained, which were washed with ether and recrystallised from alcohol. The *hydrochloride* was thus obtained in deep orange needles, m. p. 239—240° (Found : Cl, 19·6. $C_7H_6N_2S,HCl$ requires Cl, 19·1%).

ψ-Aminobenzthiazole (XVI).—The bright yellow base obtained by treating the red hydrochloride with ammonia (*d* 0·880) was dried and recrystallised from " sodium-dried " benzene at 20°, separating in slender, pale yellow needles which sintered and softened at 129° and melted to a clear purple-red liquid at 131° (Found : N, 18·4; S, 21·6. $C_7H_6N_2S$ requires N, 18·7; S, 21·3%). Its mixture with 1-aminobenzthiazole commenced to soften at 120° and melted indefinitely at about 127°. On treating the base with hydrochloric acid the red hydrochloride was at once regenerated.

ψ-Amino-3-toluthiazole Hydrochloride.—The hydrochloride from 1 g. of 1-amino-3-methylbenzthiazole (p. 1398) was suspended in 25 c.c. of alcohol and treated with 3 c.c. of ethyl nitrite solution. A *hydrochloride* was obtained as in the previous case in ruby-red prisms which sintered at 140° and showed colour change at 145° (Found : Cl, 18·0. $C_7H_8N_2ClS$ requires Cl, 18·7%). On treatment with ammonia a base similar to the previous one was obtained.

ψ-Amino-5-toluthiazole hydrochloride was obtained from 1-amino-5-methylbenzthiazole in red prisms which sintered at 130°, darkened at 140° and softened at about 150°.

The Mobility of 5-*Bromo*-1-*aminobenzthiazole.*

5-*Bromo*-1-*aminobenzthiazole dibromide*, prepared from *p*-bromophenylthiocarbamide (1 g.) and bromine (0·8 c.c.) in chloroform (10 c.c.) in the usual way, separated, on cooling, as a red gum which solidified in orange-red needles, softening at 80—82° (Found : Br, 63·5. $C_7H_5N_2Br_3S$ requires Br, 61·7%). By successive treatment with sulphurous acid and ammonia it was converted into 5-bromo-1-aminobenzthiazole, m. p. 211°, identical with the bromo-substitution product obtained by dissolving 1-aminobenzthiazole dibromide in hot water (Hugershoff, *loc. cit.*).

1-*Acetylaminobenzthiazole Hexabromide.*—1-Acetylaminobenzthiazole (0·5 g.) in chloroform (6 c.c.) was slowly treated with

bromine (0·4 c.c.), and the solution boiled after some time. The *hexabromide* crystallised from the warm liquid, on scratching, in small, orange-red prisms which, after being dried, turned yellow at 130°, lost bromine at about 140°, and became colourless at about 160° (Found: Br, 71·6. $C_9H_8ON_2Br_6S$ requires Br, 71·4%).

5-Bromo-1-acetylaminobenzthiazole.—A solution of the preceding hexabromide in alcohol was diluted with a little water and concentrated. The white, crystalline product, after treatment with dilute ammonia, crystallised from ethyl acetate in prisms, m. p. 223° (Found: Br, 30·0. $C_9H_7ON_2BrS$ requires Br, 29·5%). On hydrolysis with 50% sulphuric acid, impure 5-bromo-1-aminobenzthiazole (m. p. 184°) was obtained which melted at 198° when mixed with an authentic specimen.

5-Bromo-1-imino-2-acetyl-1 : 2-dihydrobenzthiazole.—A solution of the dibromo-addition compound of 1-imino-2-acetyl-1 : 2-dihydrobenzthiazole in alcohol was diluted with water, concentrated on a steam-bath, decanted from a small purple residue, and evaporated. The resin thus obtained became hard on treatment with ammonia and thereafter crystallised from alcohol–ethyl acetate in small plates, m. p. 199—200° (Found: Br, 30·0. $C_9H_7ON_2BrS$ requires Br, 29·5%).

On hydrolysis with 40% sulphuric acid and neutralisation, 5-bromo-1-aminobenzthiazole (m. p. 204°) was obtained; this crystallised from alcohol in prisms which, alone or mixed with 5-bromo-1-aminobenzthiazole prepared from 1-aminobenzthiazole dibromide, melted at 210°.

Homologues of 1-*Aminobenzthiazole.*

1-Amino-3-methylbenzthiazole Dibromide.—The solution obtained by treating 2 g. of *o*-tolylthiocarbamide in 20 c.c. of chloroform with bromine (1·5 c.c.) was refluxed and concentrated; on cooling, lustrous orange plates of the *dibromide* crystallised, m. p. 110° (effervescence) (Found: Br, 49·6. $C_8H_8N_2Br_2S$ requires Br, 49·4%). The dibromide was unstable and decomposed with loss of bromine on exposure to air. It dissolved in alcohol, and from the solution, diluted with water and thereafter concentrated, white needles of the *hydrobromide* of bromo-1-amino-3-methylbenzthiazole were obtained which became yellow at 260° and charred at about 290° (Found: Br, 49·8. $C_8H_7N_2BrS,HBr$ requires Br, 49·7%). The *base* obtained by treating the hydrobromide with ammonia separated from alcohol–ethyl acetate in tufts of silky needles, m. p. 212° (Found: Br, 33·1. $C_8H_7N_2BrS$ requires Br, 32·9%).

1-Amino-3-methylbenzthiazole was obtained from the dibromide by reduction with sulphurous acid and sulphur dioxide in the usual

way. It crystallised from 50% alcohol in small, lustrous plates, m. p. 136°, and resembled 1-aminobenzthiazole in odour (Found : S, 19·8. $C_8H_8N_2S$ requires S, 19·5%). The diazotised base gave a red azo-dye on coupling with alkaline β-naphthol.

1-*Amino*-5-*methylbenzthiazole Dibromide Hydrobromide.*—*p*-Tolylthiocarbamide (2 g.) was brominated in chloroform as in the previous case. The bromo-addition compound was obtained in small, glistening orange-red prisms, m. p. 134° (decomp.) after sintering at 128° (Found : Br, 59·0. $C_8H_8N_2Br_2S,HBr$ requires Br, 59·2%). The tribromide was very unstable in air. Treatment of its alcoholic solution with water produced the hydrobromide of the bromo-substitution derivative, which crystallised in silky needles. The base obtained by treatment with ammonia crystallised from alcohol (80%) in small prisms, m. p. 210° (Found : Br, 33·0. $C_8H_7N_2BrS$ requires Br, 32·9%).

By brominating *p*-tolylthiocarbamide (1 g.) in chloroform under similar conditions to the above, the tribromide was on one occasion obtained in bright red prisms, m. p. 106° (decomp.) (Found : Br, 59·5%).

1-*Amino*-5-*methylbenzthiazole*, obtained by reduction of the tribromide, crystallised from 50% alcohol in small, glistening prisms, m. p. 142°, having the usual faint odour of these bases (Found : S, 19·1. $C_8H_8N_2S$ requires S, 19·5%). The base yielded an unstable diazonium chloride which coupled with alkaline β-naphthol, giving a red azo-dye of the usual type.

1-*Amino*-4-*methylbenzthiazole Tetrabromide.*—Prepared from *m*-tolylthiocarbamide (0·3 g.) and bromine (0·4 c.c.) in chloroform (5 c.c.) in the usual way, the *tetrabromide* was obtained, either spontaneously or by cooling the solution and scratching, in slender, orange-red needles which, after being dried, became yellow at 140°, soft at 160°, white at 180°, brown at 210°, and melted and decomposed at about 250° (Found : Br, 66·8. $C_8H_8N_2Br_4S$ requires Br, 66·1%). It had the usual properties of these bromides.

1-*Amino*-4-*methylbenzthiazole.*—The tetrabromide was reduced in the usual way. The base was precipitated by making the sulphurous acid solution alkaline and a further small quantity was obtained by extracting the filtrate with ether. The base crystallised from 50% alcohol in pearly plates, m. p. 145° (sintering at 135°), having the faint characteristic odour of these compounds (Found : S, 19·2. $C_8H_8N_2S$ requires S, 19·5%).

1-*Amino*-3 : 5-*dimethylbenzthiazole Tetrabromide.*—Prepared from 1 g. of *m*-xylylthiocarbamide and bromine (0·8 c.c.) in chloroform (10 c.c.), the *tetrabromide* separated from the cooled solution in red flakes which, after being dried in a vacuum, became colourless at

80—90° and were unmelted at 250° (Found: Br, 63·8. $C_9H_{10}N_2Br_4S$ requires Br, 64·3%). It is very unstable, losing bromine and becoming colourless on exposure to air for ½ hour.

1-*Amino*-3 : 5-*dimethylbenzthiazole*, obtained from it in the usual way, crystallised from ether in needles and thereafter from dilute alcohol in silvery plates, m. p. 116° (softening at about 100°), having the usual faint odour of these compounds (Found: S, 16·8. $C_9H_{10}N_2S$ requires S, 17·9%).

2-*Amino*-β-*naphthathiazole Tetrabromide*.—Prepared from α-naphthylthiocarbamide (0·5 g.) and bromine (0·5 c.c.) in chloroform, the *tetrabromide* was obtained as an orange, microcrystalline powder which, after drying in a vacuum, began to lighten in colour at 130° and was unmelted at 260° (Found: Br, 60·9. $C_{11}H_8N_2Br_4S$ requires Br, 61·6%).

2-*Amino*-β-*naphthathiazole*, obtained by reducing the tetrabromide, crystallised from alcohol–ethyl acetate in small, odourless crystals, m. p. 235—237° after sintering at about 220° (Found: S, 16·1. $C_{11}H_8N_2S$ requires S, 16·0%).

2-*Amino*-α-*naphthathiazole Tetrabromide*.—β-Naphthylthiocarbamide (0·5 g.) was brominated as in the case of the α-compound. The *tetrabromide* was obtained as a yellow, microcrystalline powder, m. p. 165° (decomp.) (Found: Br, 60·8%).

2-*Amino*-α-*naphthathiazole* crystallised from alcohol–ethyl acetate in small prisms, m. p. 249—251°, after sintering at about 230° (Found: S, 16·2. $C_{11}H_8N_2S$ requires S, 16·0%).

The 1-*Aminobenzthiazole Dibromide* → 5-*Bromo*-1-*aminobenzthiazole Hydrobromide Transformation.*

1-Aminobenzthiazole dibromide (obtained by Hugershoff's method, *loc. cit.*; after being dried in the usual way, it turned red at 105—110°, melted at 112—114°, and charred at 206°) (36 g.) was added to 200 c.c. of nearly boiling water. A colourless solution was at once produced which on evaporation on the steam-bath left 32 g. of crude 5-bromo-1-aminobenzthiazole hydrobromide (a certain amount of the dibromide undergoes decomposition, giving the hydrobromide of 1-aminobenzthiazole). Thirty g. of the product, after treatment with ammonia and recrystallisation from alcohol, yielded 15—16 g. of 5-bromo-1-aminobenzthiazole.

In view of the curious physiological action of certain benzthiazole derivatives (J., 1925, **127**, 911), the alleged immunity to certain swamp fevers conferred by "thiazole dermatitis" (private communication from Dr. G. M. Dyson), and the clinical use of substances such as *o*-aminophenyl sulphide in syphilis, a series of

experiments has been commenced in collaboration with Dr. Dyson on the trypanocidal effect of water-soluble aminobenzthiazoles.

The author desires to express his gratitude to Professor J. F. Thorpe, F.R.S., for his kind interest in these experiments, and to the Trustees of the Dixon Fund of the University of London for a grant which has defrayed the cost of some of the materials.

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CLXXX.—*Aminobenzthiazoles. Part IV. The Stability of the Bromides of the* 1-*Xylidinodimethylbenzthiazoles.*

By ROBERT FERGUS HUNTER.

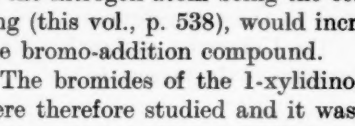
THE remarkable instability of 1-amino-3 : 5-dimethylbenzthiazole tetrabromide (this vol., p. 1389) must be attributed to the combined effects of the *o*- and *p*-methyl groups, since the stability of the bromo-addition compounds of 1-amino-5-methylbenzthiazole, 1-amino-3-methylbenzthiazole, and 1-amino-3 : 5-dimethylbenzthiazole decreases in the order given. The *o*-methyl group is mainly responsible for the instability, a fact which is further exemplified by the relative stabilities of the bromides of 1-*o*-toluidino-3-methylbenzthiazole and 1-*p*-toluidino-5-methylbenzthiazole (Hunter, J., 1925, **127**, 2023).

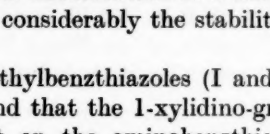
It was therefore of interest to examine the effect of replacing the amino-group in 1-amino-3 : 5-dimethylbenzthiazole by an arylamino-group. In the first place, it might be expected on *a priori* grounds that the residual affinity of the aromatic nucleus of the arylamino-group would exert a stabilising influence on the bromo-addition compound of such a base, and secondly, on the basis of Ingold's modified strain theory (J., 1921, **119**, 305 and later papers),* the bulky substituent might be expected to enhance the arylamino-

* The theoretical basis of this theory will be discussed in a paper dealing with the mobility of the 5-bromo-1-alkylaminobenzthiazole system and the addition of bromine to tautomeric systems of this type. The unsaturation of the ring nitrogen atom of the mobile triad system N:C·N[H] X⇌N[H]·C:NX is profoundly affected by the mobility or potential mobility of the tautomeric hydrogen atom. For instance, there is a striking increase in the stability of the 5-bromo-1-alkylaminobenzthiazole 2 : 2-dibromide towards hydriodic acid as the alkyl group is in turn ethyl, *n*-propyl, *n*-butyl, and *iso*butyl. In this connexion it is hoped to obtain some information on the deflexion of the carbon tetrahedral angle (Deshapande and Thorpe, J., 1922, **121**, 1430, and later papers) produced by the hitherto unstudied butyl, amyl, and hexyl groups.

phase of the mobile aminothiazole system (this vol., p. 1385) the ring nitrogen atom in which is more unsaturated than that in the 1-imino-1 : 2-dihydrothiazole form. The second effect also, owing to the nitrogen atom being the centre of unsaturation in a thiazole ring (this vol., p. 538), would increase considerably the stability of the bromo-addition compound.

The bromides of the 1-xylidinodimethylbenzthiazoles (I and II) were therefore studied and it was found that the 1-xylidino-group had a most striking stabilising effect on the aminobenzthiazole bromide complex.

(I.) 

 (II.)

(III and IV.) $C_6H_2Me_2\begin{matrix}SBr_2\\NBr_2\end{matrix}>C\cdot NH\cdot C_8H_9$

Under the usual conditions of bromination in chloroform (*loc. cit.*), *s*-di-*m*-xylylthiocarbamide readily passed into the *tetrabromide* of 1-*m*-xylidino-3 : 5-dimethylbenzthiazole (III), which is one of the most stable compounds of this type so far isolated, its stability in air being of the same order as that of the 2-β-naphthylamino-α-naphthathiazole bromides (J., 1925, **127**, 2270). The formation, in the presence of an excess of halogen, of a labile *heptabromo*-addition compound of the dimethylbenzthiazole was also observed, this compound being doubtless the hydrobromide of the hexabromo-addition compound, which was on one occasion isolated in an impure condition. These compounds were all reduced in the usual manner by sulphurous acid, yielding the xylidinodimethylbenzthiazole (I).

While these experiments were in progress, a paper by Levi (*Atti Cong. Naz. Chim. Ind.*, 1924, 400) appeared, in which 1-*m*-xylidino-3 : 5-dimethylbenzthiazole (I) was described as being formed by the thionation of a mixture of *m*-xylidine and phenyl-*m*-xylylthiocarbamide. Levi's product, however, although it gave the pure acetyl derivative, must have been very impure, because the melting point recorded is nearly 20° too low. This is not so surprising in view of the difficulties involved in such preparations (Hunter, *J. Soc. Chem. Ind.*, 1923, **42**, 302T).

Under the usual conditions of bromination, *s*-di-*p*-xylylthiocarbamide readily passed into the *tetrabromide* of 1-*p*-xylidino-3 : 6-dimethylbenzthiazole (IV), a bright red compound resembling the *m*-xylidino-isomeride in stability and other properties.

None of the 1-xylidinodimethylbenzthiazole bromides gave any evidence whatsoever of the existence of stable yellow tribromides (*loc. cit.*). Therefore, with regard to stability in the air, the 1-arylaminobenzthiazole bromides fall into two groups, the first of which includes the labile red bromo-addition compounds, such as those derived from 1-anilinobenzthiazole and its tolyl and α-naphthyl homologues, which on exposure to air evolve bromine and pass into stable yellow tribromides; and the second of which includes the stable red bromides of 2-β-naphthylamino-α-naphthathiazole and of the 1-xylidinodimethylbenzthiazoles described in this paper, which lose bromine appreciably only on prolonged exposure to moist air and do not appear to be capable of yielding yellow tribromides.

EXPERIMENTAL.

1-m-*Xylidino*-3 : 5-*dimethylbenzthiazole Hexabromide Hydrobromide.*—A solution of 1 g. of *s*-di-*m*-xylylthiocarbamide in chloroform (10 c.c.) was gradually treated with a solution of bromine (1 c.c., in chloroform, 3 c.c.) and then heated under reflux for 2 minutes, cooled, and a part of the solvent evaporated off in a vacuum at 15°. The red gum produced, which solidified, was triturated with an ethereal solution of bromine; the *heptabromide* was then obtained in small, red prisms which, after drying in a vacuum over potassium hydroxide, sintered at 153° and melted at 158° (decomp.) (Found : Br, 66·7. $C_{17}H_{18}N_2Br_6S$,HBr requires Br, 66·7%).

1-m-*Xylidino*-3 : 5-*dimethylbenzthiazole Tetrabromide* (III).—The dixylylthiocarbamide (5 g. in chloroform, 10 c.c.) was treated as above (bromine, 4·8 c.c., in chloroform, 10 c.c.) and the cooled solution allowed to crystallise in a vacuum; the *tetrabromide* was then obtained in small, orange-red crystals which, after being washed with bromine in ether and dried in a vacuum, melted at 130° (decomp.) (Found : Br, 52·7. $C_{17}H_{18}N_2Br_4S$ requires Br, 53·3%). The tetrabromide had the usual properties of these compounds, being reduced by hydriodic acid with liberation of iodine, and evolving acetaldehyde on boiling with dilute alcohol.

Bromination in similar circumstances of 5 g. of the thiocarbamide with 5 c.c. of bromine produced on one occasion a red gum which, on trituration with bromine in ether, solidified to a mass of small, red crystals, m. p. 126° after drying in a vacuum (Found : Br, 61·3. $C_{17}H_{18}N_2Br_6S$ requires Br, 62·9%).

1-m-*Xylidino*-3 : 5-*dimethylbenzthiazole* obtained in the usual way by reducing any of the bromides with sulphurous acid and sulphur dioxide (*loc. cit.*) and liberating the base with ammonia, crystallised from alcohol–ethyl acetate (1 : 1) in large flakes and thereafter

from light petroleum (b. p. 40—60°) in small prisms, both forms melting at 175° (Found : S, 11·4. Calc. : S, 11·4%).

The acetyl derivative, obtained by heating a solution of the base in acetic anhydride for a few minutes and pouring it into alcohol, slowly crystallised in large prisms, m. p. 131—132° after recrystallisation from alcohol (Levi, *loc. cit.*, gives m. p. 131°).

s-*Di*-p-*xylylthiocarbamide*.—A mixture of technical *p*-xylidine (18 g.), alcohol (27 c.c.), carbon disulphide (33 c.c.), and potassium hydroxide (4 g.) was heated for 2—3 hours, and the product worked up in the usual way; on recrystallisation from alcohol the thiocarbamide was obtained in needles, m. p. 146—147° (Dyson and George, J., 1924, **125**, 1705, give the m. p. as 148·5°). The yield was about 50%.

1-p-*Xylidino*-3 : 6-*dimethylbenzthiazole Tetrabromide* (IV).—Di-*p*-xylylthiocarbamide (1·25 g.) in chloroform was treated with bromine (1·2 c.c.) in chloroform (2·5 c.c.) in the usual way, the solution concentrated in a vacuum, and the product triturated with an ethereal solution of bromine. The red oil obtained, on partial evaporation of the ether, solidified to a mass of small, red crystals of the *tetrabromide* which were washed with chloroform and dried in a vacuum in the usual way. They had the usual properties and charred above 200° (Found : Br, 53·6. $C_{17}H_{18}N_2Br_4S$ requires Br, 53·2%).

1-p-*Xylidino*-3 : 6-*dimethylbenzthiazole*, obtained by the reduction of the tetrabromide in the usual way, crystallised from ethyl acetate in small prisms, m. p. 200° (Found : S, 11·6. $C_{17}H_{18}N_2S$ requires S, 11·4%).

In conclusion, the author desires to express his gratitude to Professor J. F. Thorpe, F.R.S., for his kind interest in this work, and to Mr. G. G. Alford for carrying out some of the experiments. A part of the expense of the materials was defrayed by a grant for which the author is indebted to the Trustees of the Dixon Fund of the University of London.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, February 9th*, 1926.]

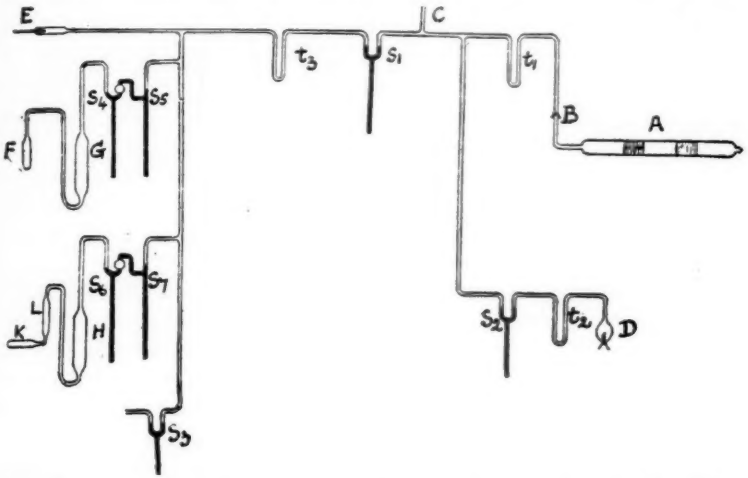
CLXXXI.—*The Direct Synthesis of Nitrous Oxide.*

By DAVID LEONARD CHAPMAN, RICHARD ALLEN GOODMAN, and RODNEY THOMAS SHEPHERD.

HITHERTO it has not been found possible to effect a direct synthesis of nitrous oxide. We shall show that this compound is slowly formed when an electric discharge is passed through nitrogen at low

pressure in a quartz tube into the walls of which oxygen has previously been driven by means of the discharge, and can be isolated as it is formed by condensing it in a U-tube surrounded by liquid air. When completely decomposed by heating a platinum wire in it, the volume increases in the ratio 2 to 3, the proportion of nitrogen to oxygen in the decomposition products being 2 to 1.

The quartz tube, A (*vide* diagram), in which the discharge took place was approximately 1 m. in length and 1180 c.c. in volume. The rest of the apparatus was of glass, and was connected to the quartz tube by a ground glass joint, B, which was lubricated with glacial phosphoric acid and sealed by mercury. The long U-tube, t_1, could be immersed in liquid air when desired, and served the



double purpose of keeping back mercury vapour and of condensing the nitrous oxide. A T-piece, C, led to the McLeod gauge used to measure the pressures. The discharge tube, with gauge and liquid-air trap, could be shut off from the rest of the apparatus by the mercury seals s_1 and s_2. The seal, s_2, served to put the quartz tube into communication with a U-tube, t_2, and a bulb, D, which contained a spiral of fine platinum wire welded to thick platinum leads, which passed to the outside through a lead–glass seal. t_3 was another U-tube which could be surrounded by liquid air. Beyond the mercury seal, s_3, was a mercury vapour pump and an auxiliary Sprengel pump. The remainder of the apparatus was for the purpose of generating and storing the gases required.

Hydrogen.—The hydrogen required for the analysis was admitted to the apparatus by diffusion through the walls of a platinum tube, E, sealed into the end of a glass tube. The platinum tube was heated

to redness in an atmosphere of hydrogen, prepared in the ordinary way in a small Kipp's apparatus from zinc and dilute sulphuric acid. The gas, after bubbling through a solution of caustic soda, was passed through a quartz tube which surrounded the platinum tube. To admit hydrogen to the apparatus the quartz tube was heated strongly.

Nitrogen.—The nitrogen was prepared by the decomposition of pure anhydrous barium azide contained in a vertical tube, F. This was connected to a reservoir, G, of capacity about 400 c.c., in which the gas was stored. One limb of the seal s_4 was blown out into a bulb, of volume about 4 c.c., the upper end being connected by millimetre capillary tubing to another seal, s_5. This arrangement was employed to withdraw small amounts of gas from the reservoir, in which the pressure was about 1 cm., in the following way. The mercury in the seal s_4 was lowered, and when raised again, shut off a small amount of gas in the bulb. The seal s_5 was then lowered until the T-piece was just cleared. The mercury in s_4 was then raised, and the gas enclosed in the bulb driven past the seal s_5 into the apparatus. By subsequently lowering the mercury in the seal s_4, the bulb could be again evacuated. The tube, F, containing the barium azide, was heated in a small bath of glycerol. The nitrogen was evolved at a convenient rate at 152°.

Oxygen.—The oxygen was prepared by the thermal decomposition of recrystallised potassium permanganate contained in the tube K. The gas passed up a tower, L, containing solid caustic potash to absorb any carbon dioxide. L was connected to a reservoir, H, and two seals, s_6 and s_7, by means of which small quantities of gas could be removed as described above in the case of nitrogen.

The gases were not admitted to the discharge tube until they had remained in that portion of the apparatus between the seals s_1, s_3, s_5, s_7, for at least ½ hour with liquid air surrounding the U-tube t_3. The gases did not come into contact with any grease taps whatever.

The Discharge.—For the purpose of exciting the discharge, two pieces of aluminium foil about 6 cm. wide were fastened by copper wire round the tube at equal distances from each end and from each other. The aluminium electrodes were connected by means of copper wire with the secondary of a 10-inch induction coil, which was run from the 100-volt mains, a resistance keeping the primary current constant at about 2¼ amp. Interruption of the primary was effected by a mercury break of the simple dipper type. The dipper was oscillated by means of an eccentric coupled directly to the shaft of an electric motor. By this means constant interruption was obtained. There was an external spark-gap of 1 cm.

To conduct an experiment, the whole apparatus was first

thoroughly evacuated, all the tubing, including the McLeod gauge, being heated twice with a blow-pipe flame, in order to drive off gases retained by the surface of the glass. The quartz tube was thoroughly heated to redness, section by section, to expel any gas that might be absorbed. The required amount of oxygen was then withdrawn from the reservoir, and admitted to the quartz tube in the manner already described. The initial pressure of oxygen was about 0·08 mm. The pressures recorded below have been reduced to the temperature of 18°, allowance being made for the cooling effect of the liquid air on the small proportion of gas contained in the U-tube t_1. After the discharge had been started, the progress of the absorption was followed by measuring the pressure at convenient intervals of time. The discharge was stopped when the pressure–time curve had become very flat. The liquid air was then removed, and the tube evacuated. Nitrogen was then admitted to a pressure of about 0·08 mm., the liquid air replaced round t_1, and the discharge again started. From time to time the discharge was stopped, and the pressure measured both with and without liquid air surrounding the U-tube t_1. The difference between these two pressures gave the amount of condensable gas formed. It was, of course, produced at a gradually decreasing rate. The results of four experiments are in Table I.

TABLE I.

Oxygen absorbed.	Nitrogen absorbed.	Condensable gas.	Duration.
0·01669 mm.	0·03777 mm.	0·01688 mm.	6¾ hrs.
0·02168	0·04282	0·02321	9¾
0·01576	0·04725	0·02999	11¼
0·01479	0·04869	0·02185	17½

When a convenient amount of gas had been obtained, the tube was evacuated, the liquid air remaining round the U-tube. A small amount of the condensable gas was always lost during this operation, showing that the liquid had an appreciable vapour pressure at the temperature of liquid air. Some experiments were made with a view to determining the properties of the gas. It was quite stable, and could be kept for any length of time. It was very rapidly destroyed by the discharge, decomposition being complete in about 5 seconds. The observed expansion was dependent on the length of time during which the discharge passed, a maximum being reached in a few seconds. The contraction which followed the expansion was probably mainly due to combination of the oxygen produced in the decomposition with mercury vapour, in the presence of which this experiment had to be performed. The gas was not condensed when the U-tube was surrounded by solid carbon dioxide and ether. It did not react with oxygen when left to stand with this

gas, showing that it could not be nitric oxide. This conclusion was confirmed by the circumstance that the gas did not attack the mercury in the McLeod gauge either before or after it had been mixed with oxygen.

Analysis.—The gas was analysed in the following way. The mercury seal s_2 was opened, and the pressure of the gas in the whole of the apparatus to the right of the seal s_1 measured. Liquid air was then placed round the U-tube t_2, and when all the gas had condensed, s_2 was closed. The liquid air was then removed, and replaced by solid carbon dioxide and ether, in order that the decomposition might be carried out in the presence of as little mercury vapour as possible. The platinum spiral was then heated to bright redness. After some hours the heating was stopped and the bulb allowed to cool. The flask containing the solid carbon dioxide and ether was removed, the seal s_2 opened, and the pressure measured both with and without liquid air surrounding the U-tube t_1. The difference between these two measurements gave the amount of condensable gas undecomposed. The difference between this and the amount originally present represented the gas decomposed. The results are in Table II.

TABLE II.

	Mm.
Pressure after decomposition, with liquid air	0·03746
Pressure after decomposition, without liquid air	0·03948
Condensable gas undecomposed	0·00202
Initial amount of condensable gas	0·02661
Condensable gas decomposed	0·02459
Expansion on decomposition	0·01287

It will be seen that, within the limits of experimental error, the expansion is equal to half the amount of condensable gas decomposed.

The next analysis was made in such a way as to enable the amount of oxygen produced by the decomposition to be determined. When this was known, the relative proportions of oxygen and nitrogen in the condensable gas could be calculated.

The ratio of the volume of the quartz tube *plus* tubing up to the seals s_1 and s_2, to the total volume when s_2 was opened, was first determined by measuring the pressure of the same amount of gas in the two volumes. The decomposition was then carried out in the same manner as before. While this was proceeding, hydrogen was admitted to the quartz tube, and its pressure measured. From the ratio of the volumes, the pressure this gas would produce in the total volume when s_2 was opened was calculated. After decomposition, the mercury in s_2 was lowered, and the pressure measured, as in the former case, with and without liquid air surrounding the

U-tube t_1. The pressure of the products of decomposition was found by subtracting the pressure of the hydrogen from the total pressure measured after decomposition with liquid air surrounding the U-tube. t_2 was then immersed in liquid air, and the spiral heated for several hours until no further fall in pressure occurred. From the contraction due to the formation of water, the amount of oxygen present was deduced. The nitrogen was found by difference. The results are in Table III.

TABLE III.

(a) *Expansion on decomposition.*

	Mm.
Pressure after decomposition, with liquid air	0·05998
Pressure after decomposition, without liquid air	0·06064
Condensable gas undecomposed	0·00066
Initial amount of condensable gas	0·02156
Condensable gas decomposed	0·02090
Pressure of hydrogen admitted to quartz tube	0·03001
Ratio of volumes, quartz tube : total	0·9719
Pressure of hydrogen in total volume	0·02917
Pressure of nitrogen, hydrogen, and oxygen	0·05998
Pressure of products of decomposition	0·03081
Expansion produced by decomposition	0·00991

(b) *Estimation of oxygen.*

Initial pressure (hydrogen, nitrogen, and oxygen)	0·05998
Final pressure (excess hydrogen and nitrogen)	0·02891
Contraction	0·03107
Amount of oxygen required for this contraction	0·01036

(c) *Summary.*

Condensable gas decomposed	0·02090
Oxygen produced	0·01036
Nitrogen produced	0·02045

The expansion produced on decomposition is again seen to be half the amount of condensable gas destroyed, and the ratio of nitrogen to oxygen in the products is 2 to 1, leaving no doubt that the gas was nitrous oxide.

In experiments not described above, a small proportion of oxygen was added to nitrogen in the discharge tube. Even when the partial pressure of the oxygen was as small as one-tenth of that of the nitrogen, nitrogen peroxide was produced.

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CLXXXII.—*Resins in Coal. Studies in the Composition of Coal.*

By WILFRID FRANCIS and RICHARD VERNON WHEELER.

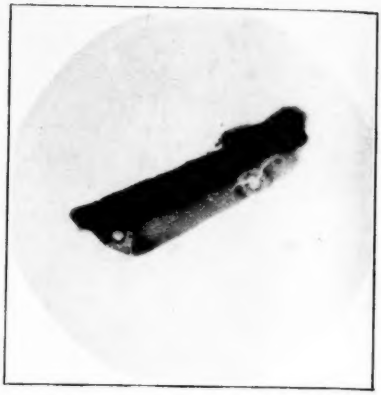
WE have shown (J., 1925, **127**, 112) that bituminous coal consists essentially of ulmin compounds in which morphologically organised plant-tissues, that have escaped ulmification, are dispersed. The ulmins, when first formed as the products of mouldering decay of vegetable matter, are characterised by ready solubility in alkaline solutions, but their derivatives, in the condition in which they normally exist in bituminous coal, are insoluble. Solubility in alkaline solutions can, however, be conferred on the ulmin compounds of bituminous coal by such mild oxidation as is afforded by treatment with air at low temperatures (up to 150°) or with hydrogen peroxide. The soluble ulmins so produced, which we have termed "regenerated" ulmins, are not identical in character with the insoluble ulmins in newly-won bituminous coal, for the external groupings of the molecules are modified during oxidation, the more easily detached being eliminated to form simple oxygenated compounds, with the substitution of carboxylic groupings which render the residue definitely acidic in character. The nuclear structure, however, remains unaffected. This nucleus we have shown (J., 1925, **127**, 2236) to be built up of compact systems of benzenoid groupings connected together by heterocyclic structures, such as pyrrole and furan or their derivatives.

The bulk of bituminous coal consists of ulmins having molecular structures of this character. In banded bituminous coals, such as constitute the majority of British coals, the dull (durain) bands contain a proportion, usually between 20 and 30%, of morphologically organised plant entities, amongst which spore exines and cuticles predominate, that have undergone but little change from their original condition during the processes of decay suffered by the accumulations of plant material from which the coal was formed. Of the bright portions of coal, the clarain contains but small proportions, up to about 5%, of such plant entities, whilst the vitrain contains none.

In our previous papers we noted that, for the sake of simplicity, the existence in coal of natural plant substances devoid of morphological organisation, such as "resins," could be ignored, but expressed the intention of dealing with these substances separately. In order to do so, it is necessary for us to enlarge on the statement, contained in a footnote to our paper on the constitution of the coal ulmins (*loc. cit.*, p. 2236), regarding the character of vitrains; for the

× 330

FIG. 1.



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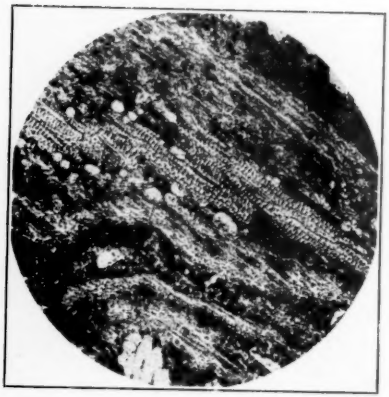
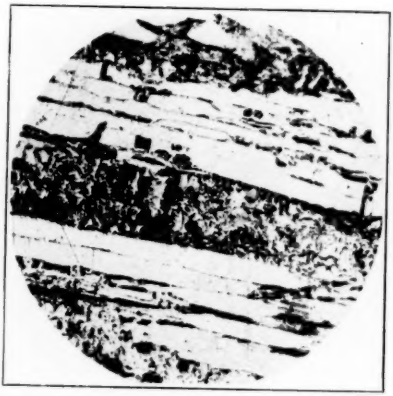


× 130

FIG. 2.



× 130

FIG. 3.

× 150

FIG. 4.

[To face p. 1411.]

existence of resins in a bituminous coal is best revealed in the vitrain portion.

The vitrain portion of a banded bituminous coal has for long been considered by British investigators to be essentially structureless, having been so qualified in Stopes's original descriptions of the banded ingredients of bituminous coal (*Proc. Roy. Soc.*, 1919, *B*, **90**, 470), based largely on an examination of transparent sections. Partly through the use of a new method of examining, by reflected light, coal surfaces that have been polished and etched, and partly as the result of the remarkably fine technique for the preparation of transparent sections of coal developed by Dr. R. Thiessen, of the United States Bureau of Mines, who has been good enough to prepare for us sections of a number of specimens of vitrain from British coals, it is now realised that a completely structureless vitrain, if it exists at all, is a rarity.

A description of the structures to be observed in most vitrains is reserved for another communication. It will suffice here to state that, in all of the many examples of vitrain that we have examined, the appearance of plant cells, usually derived from cortical tissues, can be disclosed. We purposely refer to the " appearance " of plant cells, because these structures cannot be separated from the coal mass intact and preserved, as can the cuticles and spore exines, and it is clear that, being ulmins, they are pseudomorphs of the original structures.

For the work described in this paper, vitrain from the Hamstead coal, which we have used for much of our previous work, was chosen because its oxidation by hydrogen peroxide could readily be controlled. During a carefully regulated oxidation of Hamstead vitrain, the soluble " regenerated " ulmins being removed from time to time by means of dilute sodium hydroxide solution, it was found that, when but little residue remained, the particles began to assume distinctive shapes. Some of the particles had the appearance of fibre cells, whilst in a few the shapes of tracheids, showing bordered pits, could be observed. All such shapes were, however, transient, disappearing as the ulmins dissolved. Nevertheless we were able to secure examples and retain them long enough to photograph them under the microscope. Some are reproduced in Fig. 1.

The fragments to which, from the point of view of the present paper, the greater interest attaches, were dark-coloured and elongated. They were usually ribbed along their major axes and had clean-cut ends. On persisting with the action of hydrogen peroxide, followed by treatment with sodium hydroxide solution, these fragments became gradually lighter in colour and finally, when all the ulmins had been removed, appeared as yellow rods varying in length

up to 0·02 inch. Their diameter was about one-tenth of their length.

From their general character and from the cellular appearance of the ulmin material surrounding them, there seems little doubt but that these rods were resin inclusions. A number of them were collected and extracted in a Soxhlet fat-extraction apparatus with chloroform, in which they were almost completely soluble, when a dark yellow semi-solid extract was obtained. The analytical results (Found: C, 80·6; H, 10·3%) are consistent with the assumption that the material was a resin.

Confirmation of the suggestion that the resin rods existed in this sample of Hamstead vitrain in the position that they had occupied in the woody tissues from which the vitrain was formed is obtainable from photomicrographs of portions of the same sample of vitrain as was used for the oxidation experiments, polished and etched with chromic and sulphuric acids. Two such photographs are reproduced in Figs. 2 and 3, the magnification in each instance being 130 diameters. In Fig. 2, the surface is at right angles to, and in Fig. 3 it is parallel with, the cell-walls. The resin inclusions appear as circular patches in Fig. 2 and as rods in Fig. 3.

The cellular structure that abounds in vitrain—in the present example it is of xylem—can be clearly seen in the photographs, and it may well be asked how such structures could have escaped notice. Although they are readily rendered visible by polishing and etching a vitrain surface, a method of examination that has but recently come into use, the structures are difficult to detect in a transparent section viewed by transmitted light, because they are not outlined on the transparent reddish-brown background by a contrasting colour, but are faintly visible (and then only when the section is exceedingly thin and well illuminated) by reason of slight differences in shade. For example, a photograph of a section (× 150) of the same sample of vitrain as was used for Fig. 2 is reproduced in Fig. 4. The circular patches so noticeable in Fig. 2 can be recognised, but no organised structures can be detected.

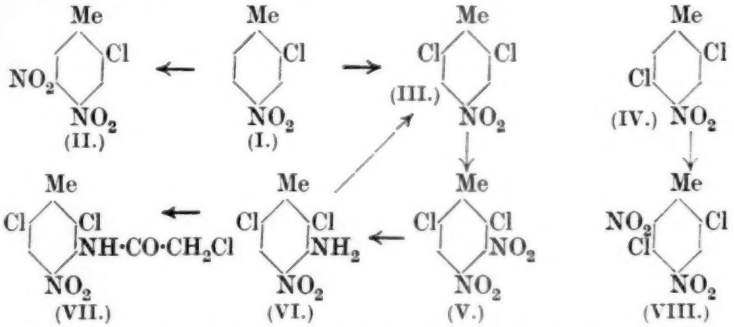
We are indebted to Miss M. M. Evans, of the Fuel Research Board's staff, for the preparations illustrated in Figs. 2 and 3, and to Dr. R. Thiessen for that illustrated in Fig. 4. Our thanks are also due to the Safety in Mines Research Board for permission to publish this paper.

SAFETY IN MINES RESEARCH BOARD,
SHEFFIELD. [*Received, April 22nd,* 1926.]

CLXXXIII.—*A Study of the Rule of the Conservation of the Type of Substitution in Aromatic Substances. Part I. Chlorination of 2-Chloro-4-nitrotoluene.*

By WILLIAM DAVIES and GEOFFREY WINTHROP LEEPER.

MORGAN and DREW (J., 1920, **117**, 793) have shown that the main product (more than 85%) of nitration of 2-chloro-4-nitrotoluene (I) is the 5-nitro-derivative (II). It was shown by one of us (J., 1922, **121**, 806) that, when (I) was chlorinated in the presence of certain catalysts, not the 5- but the 6-chloro-derivative (III) was produced in a yield of more than 30%, and no other isomeride was isolated in a pure condition. It was accordingly stated (p. 806) that "it is very probable that the separation of (III) in such large amount indicates that this is the chief product." Holleman (*Chemical Reviews*, 1924, 217) quite rightly points out that (III) had not been proved to be the principal product of the reaction, and considers it possible that (IV) may occur in the residual non-crystallisable oil in such large amount as actually to be the chief product of the reaction. As changes in substitution type are of great importance both from the synthetical and the theoretical point of view, an attempt has been made to determine more accurately the proportion of (III) formed.



The more obvious lines of attack have already been investigated (Davies, *loc. cit.*, p. 810) without success. As the monochlorination product of (I) is clearly an extremely complicated mixture, the method of estimation suggested by Holleman (*loc. cit.*, p. 217) was not adopted, but instead attempts were made to convert (III) into a derivative which could be separated from the mixture by chemical means. It is to be expected that (III) would be rather more easily substituted than (IV), and the behaviour of certain reagents on (III) was accordingly examined. It was not readily sulphonated, but was quantitatively converted into the nitro-derivative (V) by

nitration under mild conditions. This could not be smoothly converted into a nitrophenol by the action of alkali under various conditions, but it was readily transformed by the action of alcoholic ammonia into (VI) (the yield of pure substance being 77%), and insufficient of the isomeric 2 : 6-dichloro-3-nitro-*p*-toluidine was formed to admit of its being isolated. This change is incidentally still another instance of replacement in agreement with the rule of Kenner and Parkin (J., 1920, **117**, 852. See also J., 1925, **127**, 2344).

2: 6-*Dichloro*-4-*nitro*-m-*toluidine* (VI) has very slight basic properties and accordingly attempts were made to convert it into an acidic substance. It does not react with *p*-toluenesulphonyl chloride, and although good yields of the benzoyl and acetyl derivatives of the amine may be obtained, these compounds do not dissolve very readily in cold dilute alkali. The *chloroacetyl* derivative (VII), however, is quantitatively obtained, and easily dissolves in cold aqueous sodium hydroxide solutions, from which it is precipitated unchanged on acidification. It was hoped to be able to separate in this way (V) from (IV) or its nitro-derivative (VIII) (compare Cohen and Dakin, J., 1901, **79**, 1131).

The chlorination product from (I) was therefore nitrated under the gentle conditions which were sufficient to give (V), and after the removal of the catalyst the whole product was treated with alcoholic ammonia, but it was then found that some portion of the nitration product other than (V) gave amines with ammonia with the formation of large quantities of ammonium chloride. It is possible that the 5-chlorine atom in (VIII) had, despite the steric hindrance due to the two adjacent nitro-groups, reacted with the ammonia. As the chloroacetyl derivatives of the amines produced were themselves soluble in alkali, this method of separation by chemical means was abandoned.

Finally, crystallisation from methylated spirit of the nitration product of the chlorination mixture was resorted to, and 2 : 6-dichloro-3 : 4-dinitrotoluene (V) was isolated in a yield corresponding to 47·9% of 2 : 6-dichloro-4-nitrotoluene (III) in the chlorination product. This physical method of separation, although far from being an ideal one, makes it certain, when considered in connexion with the following facts, that (III) is the chief dichloronitrotoluene formed. First, it is impossible to separate by fractional crystallisation all the (V) produced, owing to the formation of liquid and low-melting solid mixtures of a complex nature. Secondly, it has been shown (Davies, *loc. cit.*, p. 810) that the monochlorination of (I) with the calculated amount of chlorine left some unchanged substance, and therefore that one or more trichloro-*p*-nitrotoluene derivatives were formed. In fact, a larger amount of (V) can be isolated

when the chlorine absorbed is about 1% greater than the quantity theoretically required to produce dichloro-*p*-nitrotoluenes (see p. 1417). Hence the monochlorination product of (I) contains considerable quantities of substances other than dichloro-*p*-nitrotoluenes.* Moreover, there is reason to believe that a portion of the chlorine goes into the side chain. On monochlorination of (III) in presence of either antimony trichloride or ferric chloride, a very complex mixture is formed from which nothing pure can be isolated by distillation or crystallisation, although mono-substitution could lead only to 2 : 5 : 6-trichloro-4-nitrotoluene. Nitration and reduction followed by condensation with phenanthraquinone gives only a small quantity of a phenanthrazine (m. p. 343°), which is possibly derived from 2 : 5 : 6-trichloro-4-nitrotoluene. It is certain from this experiment that the expected nuclear substitution of (III) has not occurred smoothly, and no doubt this anomalous reaction, whatever it may really be, occurs to some extent in the chlorination of the simpler 2-chloro-4-nitrotoluene. Side-chain substitution in presence of a catalyst is not so rare as is usually considered. One such instance, with 2-chloro-4-nitrotoluene, has already been pointed out (J., 1922, **121**, 812), with iodine as the catalyst. The present authors find that the action of bromine on *p*-nitrotoluene at 95—120° (this relatively high temperature being necessary to bring about a reaction) gives a 46% yield of pure *p*-nitrobenzyl bromide (m. p. 99°), and a similar result with toluene in presence of antimony tribromide and bromine is recorded by van der Laan (*Rec. trav. chim.*, 1907, **26**, 1).

It is difficult to advance a logical and satisfactory explanation which will account for a change of substitution type such as the one here established. As has been already pointed out (Davies, *loc. cit.*, p. 809), steric conceptions based on the atomic volumes of the groups whose positions of substitution are compared lead to contradictory conclusions, though Holleman (*loc. cit.*, p. 220) apparently considers the application of such ideas helpful as far as some rather simpler molecules are concerned. A more satisfactory, although far from convincing explanation may be found in a consideration of the difference in chemical nature of the two groups under comparison, and also in the experimental conditions of the

* In the actual experiments herein described, *p*-nitrotoluene was dichlorinated and 2-chloro-4-nitrotoluene was not first isolated and monochlorinated (see Davies, *loc. cit.*, p. 810, for the justification of this). In any case, the other possible isomeride, 3-chloro-4-nitrotoluene, could on further chlorination give no 2 : 6-dichloro-*p*-nitrotoluene, and therefore the dichlorination of *p*-nitrotoluene could not, when compared with the monochlorination of 2-chloro-4-nitrotoluene, favourably affect the proportion of 2 : 6-dichloro-3 : 4-dinitrotoluene (V) actually isolated.

reactions. Investigations are being carried out with special reference to these points of view.

EXPERIMENTAL.

2 : 6-*Dichloro*-3 : 4-*dinitrotoluene* (V).—A solution of dry 2 : 6-dichloro-4-nitrotoluene (III) (6·7016 g.) in concentrated sulphuric acid (33 c.c.) at 65° is treated with a mixture of nitric acid (3·3 c.c.; *d* 1·52) and concentrated sulphuric acid (17 c.c.). The temperature is kept at 80—85° for 8 minutes. The oil that has separated then solidifies and, after drying over phosphorus pentoxide in a cathode-ray vacuum, weighs 8·1517 g. (yield 99·8%). Its m. p., 129—130°, is raised only 1° by repeated crystallisation. Further exposure to a cathode-ray vacuum causes a steady loss in weight due, as shown by a blank experiment with pure dry material, to the volatility of the substance.

The oxidisable *o*-diamine obtained by reducing 2 : 6-dichloro-3 : 4-dinitrotoluene with zinc dust in dilute alcohol containing a trace of ammonium chloride was characterised as 1 : 3-*dichloro*-2-*methylbenzophenanthrazine*, yellowish-brown plates from anisole, m. p. 279—286° (corr.), by condensation with phenanthraquinone in glacial acetic acid. The azine is sparingly soluble in cold organic solvents and develops a cerise coloration in cold concentrated sulphuric acid (Found: Cl, 19·3. $C_{21}H_{12}N_2Cl_2$ requires Cl, 19·5%). The conversion of (V) into this compound is, however, not a quantitative process and, moreover, does not lend itself to the rough estimation of (V) in the presence of other *o*-dinitro-compounds of toluene.

2 : 6-*Dichloro*-4-*nitro*-m-*toluidine* (VI).—A mixture of 2 : 6-dichloro-3 : 4-dinitrotoluene (50 g.) and 200 c.c. of alcoholic ammonia (5%) is heated for ½ hour at 90—98° (10 atm.). The pressure is then released, 50 c.c. of alcoholic ammonia (10%) are added, and the mixture is heated for 2 hours at 127° and 7·3 atm. The product is allowed to crystallise, and after recrystallisation from alcohol 34 g. (77% yield) of the pure amine are obtained, only a small amount of low-melting material and a mere trace of ammonium chloride being produced. 2 : 6-*Dichloro*-4-*nitro*-m-*toluidine*, m. p. 136°, forms thin, deep yellow plates from benzene and brown prisms from alcohol and is soluble in mineral acids only if very concentrated (Found: Cl, 31·75. $C_7H_6O_2N_2Cl_2$ requires Cl, 32·1%). It is different from the only other possible isomeride, 2 : 6-dichloro-3-nitro-*p*-toluidine (m. p. 130—131°; Davies, *loc. cit.*, p. 814), and is converted through its diazonium sulphate into 2 : 6-dichloro-4-nitrotoluene in good yield. Its constitution is thus established.

2 : 6-*Dichloro*-4-*nitroaceto*-m-*toluidide*, obtained by boiling the base

and excess of acetyl chloride in benzene for 9 hours, separates from alcohol or benzene in colourless plates, m. p. 185°. The *benzoyl* compound, similarly prepared, forms colourless, feathery crystals, m. p. 215° (Found : N, 8·7. $C_{14}H_{10}O_3N_2Cl_2$ requires N, 8·6%). 2 : 6-*Dichloro*-4-*nitrochloroaceto*-m-*toluidide* (VII), also similarly prepared, separates from alcohol in colourless plates, m. p. 170° (Found : N, 9·4. $C_9H_7O_3N_2Cl_3$ requires N, 9·4%).

The mixture formed by dichlorinating *p*-nitrotoluene is nitrated under the conditions described on p. 1416, the product thoroughly washed with water and heated with alcoholic ammonia under the conditions described on p. 1416. The final product, containing much ammonium chloride, and amines formed by elimination of chlorine and a nitro-group, is treated with excess of benzene, the benzene–alcohol constant-boiling mixture removed on the water-bath, the dry amine chloroacetylated in benzene, the benzene and excess of chloroacetyl chloride are removed, ultimately in a vacuum, and the chloroacetylated amines extracted with cold sodium hydroxide solution and reprecipitated with cold hydrochloric acid. The product, however, melts below 158°, and is a mixture of chloroacetylated amines, from which, after three recrystallisations from alcohol, (VII) is isolated in a quantity corresponding to a yield of less than 40% of (III).

Estimation of 2 : 6-*Dichloro*-4-*nitrotoluene* (III) *as* 2 : 6-*Dichloro*-3 : 4-*dinitrotoluene* (V).—In the preliminary experiments 1 g.-mol. (137 g.) of *p*-nitrotoluene was chlorinated in the presence of antimony trichloride until, after the removal of chlorine and hydrogen chloride, the increase in weight (69 g.) corresponded closely (within 0·2 g.) to the entry of 2 gram-atoms of chlorine. After nitration, and separation of (V) by repeated crystallisation from methylated spirit, the oily residue was distilled in steam, and the least volatile portion fractionally crystallised from alcohol. The product (2 g., m. p. 85·5°) was shown by a mixed melting-point determination to be 2-chloro-4 : 5-dinitrotoluene (II). The yield of (V) corresponded to a yield of 43% of (III), and it was found advantageous to have a slight excess of chlorine over the 2 gram-atoms theoretically required, because the trichloronitrotoluene derivatives did not appear to interfere in the separation of (V) to the same extent as did (II).

One g.-mol. of *p*-nitrotoluene (137 g.) mixed with 4·5 g. of antimony trichloride is chlorinated at 65—75° until the weight is 212·7 g. A current of dry air is blown through the liquid at 100° until all the chlorine and hydrogen chloride are removed. The increase in weight is now 0·7 g. in excess of the 69 g. theoretically required. A solution of exactly half the product (105·6 g.) in concentrated sulphuric acid (350 c.c.) is treated at 65° with a

mixture of nitric acid (20 c.c.; *d* 1·52) and concentrated sulphuric acid (50 c.c.). Having been kept at 80—85° for 8 minutes, the mixture is poured on to ice, and kept for 48 hours at 0°. The solid product is then washed with cold water and boiled with methylated spirit (300 c.c.), the solution (A) poured off, and the residue dissolved in a further 300 c.c. of alcohol (Solution B). After 5 hours, (B) deposits almost pure (V), and the filtrate is used to dissolve the less pure crystals from (A). The deposit from (B) is recrystallised from methylated spirit, pure (V) being produced (m. p. 130—131°), and the filtrate is used to crystallise the much less pure portions; when the m. p. of these has been raised to 125—128°, they are crystallised from spirit. The process is expedited by pouring off the mother-liquor from the first crop of crystals, which contains the largest amount of (V), while the solution is hot. (V) is the least soluble substance present. In this way more than 50 g. of a pure product (m. p. 130—131°) are obtained in a very short time; further small quantities are obtained from the intermediate fractions. The large volume of solution containing the most soluble portion, when concentrated and kept for several months, deposits a solid from which a very small quantity of (V) can be isolated. In the first experiment, which lasted a week, 56·8 g. of (V) were isolated, corresponding to a yield of 45·2% of (III). In the second estimation, which, owing to the more thorough examination of the oily portions, was more prolonged, 60·1 g. [corresponding to a yield of 47·9% of (III)] were obtained and there were indications that a small quantity of (V) still remained in the oily mixture.

The semi-solid final product was recrystallised from alcohol and, apart from a large quantity of oil, two crystalline fractions, m. p. 85—97° and 100—115°, were obtained. The second substance softened at 100—101°, which is the m. p. of (VIII), but this compound could not be obtained pure. It (4 g.) was reduced as described on p. 1416, and the amine obtained was condensed with phenanthraquinone (2 g.) in boiling acetic acid. The product formed yellowish-brown needles (0·85 g.), m. p. 307—309° (decomp.; corr.), from anisole and gave a cerise coloration with cold concentrated sulphuric acid (Found: Cl, 23·6%). Whatever this compound may be, its formation shows that almost all (V) has been removed from the 100—115° fraction (about 9 g.). The high percentage of chlorine, much greater than that required for the phenanthrazines from (II) and (V), shows that probably a trichloronitrotoluene derivative is present.

Chlorination of 2 : 6-*Dichloro*-4-*nitrotoluene* (III).—This compound (41·2 g.), mixed with ferric chloride (1·8 g.), is chlorinated at 65—80°

for 24 hours, the increase in weight being 7·8 g. (calc. for monochlorination, 6·9 g.). The high temperature of 80° is ultimately required, not only to expedite the process, but also to melt the solid which crystallises out towards the end of the reaction. The product after removal of inorganic matter distils at 135—155°/5 mm. The colourless distillate is crystallised from spirit, and the portion (7 g.) which melts over the lowest range (60—78°) is nitrated with mixed sulphuric and nitric acids, the product reduced as described on p. 1416, and the base produced condensed with an excess of phenanthraquinone in glacial acetic acid. The compound (1·3 g.) produced separates from anisole, in which it is very slightly soluble in the cold, in deep yellow prisms, m. p. 343° (corr.) (Found : Cl, 26·6. $C_{21}H_{11}N_2Cl_3$ requires Cl, 26·8%), and may be 1 : 3 : 4-*trichloro*-2-*methylbenzophenanthrazine*, which would be the expected product if nuclear substitution had taken place in the chlorination. It is not easy, however, to understand why such a small quantity of it is formed, and why the chlorination does not proceed, as would be expected, to give 2 : 5 : 6-trichloro-4-nitrotoluene as the chief product. A pure substance could be obtained neither from the chlorination product nor from the nitration product of this by repeated crystallisation.

This phenanthrazine is different from that obtained from the highest-melting substance [after the removal of (V)] formed in the nitration of the dichlorination product of *p*-nitrotoluene. The lower-melting portions of this product, which almost certainly contains several 3 : 4-dinitrotoluene derivatives, were not examined from the point of view of the formation of phenanthrazine derivatives.

Summary.

The product of monochlorination of 2-chloro-4-nitrotoluene in presence of antimony trichloride, from which more than 30% of 2 : 6-dichloro-4-nitrotoluene had previously been isolated (J., 1922, **121**, 806), has now been shown to contain, in addition to considerable quantities of substances other than nuclear-substituted dichloro-4-nitrotoluenes, 47·9% of that compound, estimated as 2 : 6-dichloro-3 : 4-dinitrotoluene. This result, when compared with the nitration of 2-chloro-4-nitrotoluene (Morgan and Drew, J., 1920, **117**, 793), in which more than 85% of the product is 2-chloro-4 : 5-dinitrotoluene, shows that a change of substitution type has occurred.

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MELBOURNE UNIVERSITY. [*Received, January 18th*, 1926.]

CLXXXIV.—*The Boiling Points of Some Higher Aliphatic* n-*Hydrocarbons.*

By FRANCIS FRANCIS and NORMAN EDWARD WOOD.

THE long-continued fractionation of Scotch paraffin wax led to the isolation of seven fractions of constant boiling point (J., 1922, **121**, 1529), and later (*loc. cit.*, p. 2804), evidence was advanced for the belief that these fractions were pure hydrocarbons. Piper and his students (J., 1925, **127**, 2194) submitted these hydrocarbons to *X*-ray analysis, and finding that the spacings coincided with those obtained by Müller and Saville for synthetic hydrocarbons (*loc. cit.*, p. 600), concluded that "the hydrocarbons obtained from paraffin wax are identical in constitution with the synthetic *n*-hydrocarbons."

Certainly, then, as regards the material obtained from shale in Scotland fusing between 55° and 56°, and most probably paraffin from all sources, the view that has been held since Krafft's work in 1888 has been proved finally to be correct. The number of hydrocarbons present in different paraffins is still an open question, but if Scotch wax is at all typical, the number is not so large as Krafft stated, and is much nearer 10 to 12 than the 35 (18 of which were considered to be pure) that he believed to be present in the specimen he investigated (*Ber.*, 1907, **40**, 4779).

In Piper's communication, the question was raised of the untrustworthiness of the molecular magnitudes of some of the hydrocarbons from paraffin wax as determined by the ordinary ebullioscopic methods.

We thought it most probable that a direct comparison of the boiling points of synthetic *n*-docosane, $C_{22}H_{46}$, with fraction B over a range of pressures would show either that these two substances were identical, which Piper states to be the case, or that B was $C_{23}H_{48}$, the deduction from a series of very concordant molecular-weight determinations by the ebullioscopic method. *n*-Docosane was synthesised by the electrolysis of a solution of potassium laurate "Kahlbaum" (Petersen, *Z. Elektrochem.*, 1906, **12**, 141) and purified by three crystallisations from benzene; it fused at 44·5° and the specimen used for this work boiled at a constant temperature.

A boiling-point graph drawn from the data (Table I) for this synthetic material showed that all the boiling points at different pressures of the hydrocarbon B isolated from paraffin fell on that curve. There can therefore be no doubt that the two substances are identical, that one of the constituents of paraffin is

n-docosane, and that the molecular-weight determination of this hydrocarbon from that source was too high by about 4%.

TABLE I.

Boiling points at various pressures (uncorr.).

Fraction.							
B ($C_{22}H_{46}$).		C ($C_{24}H_{50}$).		E ($C_{26}H_{54}$).		F ($C_{28}H_{58}$).	
27·1 mm.	236°	27·6 mm.	255·5°	26·5 mm.	269°	28·0 mm.	288°
16·0	224	13·3	238·5	14·2	257	12·1	267·5
9·9	212	4·4	210·5	8·4	245·5	7·1	258·5
4·8	199·5	2·5	202	4·4	233	3·6	244
2·0	189	1·5	195	2·1	223·5		

Fraction.					
G ($C_{29}H_{60}$).		C.O. ($C_{24}H_{50}$).		F.O. ($C_{28}H_{58}$).	
19·0 mm.	290·5°	24·6 mm.	253°	26 mm.	287°
13·6	279·5	12·5	236·5	14·9	274·5
8·3	270·5	7·3	221	7·1	258·5
4·1	254	3·7	209	4·5	247
2·5	248			2·2	234

Synthetic Hydrocarbons.							
$C_{16}H_{34}$.		$C_{22}H_{46}$.		$C_{30}H_{62}$.		$C_{34}H_{70}$.	
19·5 mm.	161·5°	24·7 mm.	233·5°	30·5 mm.	311·5°	30 mm.	337·5°
13·8	156	18·3	226	20·5	300	19·5	325
9·0	145	11·2	215	14·5	291	15·0	319
5·3	137	5·0	198	6·2	268	4·6	297·5
				1·7	241·5	2·4	285

The synthetic hydrocarbons (C_{24}, C_{25}, C_{26}, C_{28}, C_{29}, C_{31}) required to make a similar direct comparison between the other six hydrocarbons isolated from paraffin were not available.

Consequently we synthesised *n*-hexadecane, *n*-triacontane, and *n*-tetratriacontane in order to obtain the relationship between the boiling points at 15 mm. of these hydrocarbons and their respective carbon contents. This would enable a comparison to be made with the boiling points under the same pressure of the hydrocarbons isolated from paraffin.

Hexadecane was prepared by the reduction of cetyl iodide and purified by treatment with concentrated sulphuric acid; it showed a constant boiling point of 156°/13·8 mm. Triacontane and tetratriacontane were synthesised by the electrolysis of the potassium salts of palmitic and stearic acids, respectively, these acids being the purest obtainable from Kahlbaum. Each hydrocarbon was purified by three crystallisations from benzene and the specimens used in this investigation had constant boiling points.

From the data for the synthetic hydrocarbons in Table I, the boiling points at 15 mm. can be obtained by interpolation, and when these were plotted against their respective carbon contents a smooth curve resulted.

On this curve, within an experimental error of between 1° and 2°, lay the boiling points at 15 mm. of the following hydrocarbons isolated from paraffin: $C_{24}H_{50}$, $C_{26}H_{54}$, $C_{28}H_{58}$, $C_{29}H_{60}$. We had insufficient amounts of the hydrocarbons $C_{25}H_{52}$ and $C_{31}H_{64}$ from paraffin to determine the boiling points with any degree of accuracy.

As these results are in entire agreement both with the molecular weights of these paraffin hydrocarbons as determined by the Menzies and Wright apparatus (J., 1925, **127**, 2194) and with those obtained by *X*-ray analysis, there can be no doubt that the paraffin wax investigated in these laboratories contains in addition to *n*-docosane, the *n*-hydrocarbons tetracosane, hexacosane, octacosane, and nonacosane. The two (pentacosane and hentriacontane) whose boiling points at 15 mm. have not been determined had been analysed by *X*-rays and can clearly be added to this list.

It has been shown (J., 1922, **121**, 2808) that on the oxidation of the seven hydrocarbons obtained from paraffin, in each case the small amounts which escaped this process were identical with the hydrocarbon used, and this fact was taken as a criterion that pure specimens had been isolated. Sufficient amounts of the unchanged hydrocarbons from the oxidation of tetracosane and octacosane (from paraffin) were available for the purpose of determining their boiling points at different pressures; in both cases these lay on the graphs for the parent hydrocarbons (see Table I, Fractions C.O. and F.O.). This constitutes a further proof of their identity and an additional support for the view that the two hydrocarbons are pure materials.

All the boiling points given in Table I were determined in an apparatus similar to that used for the fractionation of wax (J., 1922, **121**, 1529), but the data obtained were not corrected for the exposed stem of the thermometer.

Krafft prepared a large number of synthetic *n*-hydrocarbons in 1882 and 1886 (*Ber.*, **15**, 1687, 1711; **19**, 2218), and we found that the boiling points at 15 mm. recorded by him for the ten hydrocarbons $C_{15}H_{32}$ to $C_{24}H_{50}$ fell on the graph (connecting b. p. and carbon content) constructed from our more limited data. Even in the case of $C_{27}H_{56}$, $C_{31}H_{64}$, $C_{32}H_{66}$, and $C_{35}H_{72}$, the difference was only + 2°.

This correspondence with our uncorrected data was so striking that we concluded that Krafft's boiling points at 15 mm. could not have been corrected for the exposed stem of the thermometer. It appeared to us that the corrections, certainly necessary for our own data, were equally applicable to his.

On the thermometer used in this work and with the same appa-

ratus the boiling point of naphthalene at 744·2 mm. was 211·1°, and of benzophenone 293·5° at 749 mm. Dimmer's formula for the correction (Landolt-Bornstein, ii, 1212) being applied, these data become 216·9° and 305·9° at 760 mm., which are in agreement with the recorded boiling points of these substances, *viz.*, 217·2° and 305·9°. The correction amounts to 1·7° at 150°, 4·5° at 200°, 8·3° at 250°, and 12·3° at 300°.

In Table II are the most probable corrected boiling points at 15 mm. of Krafft's hydrocarbons and those described in this communication; the error, we believe, does not exceed ± 1·5°.

TABLE II.

Boiling points of n-*hydrocarbons* (*corrected*) *at* 15 *mm.; probable accuracy* ± 1·5°.

$C_{18}H_{32}$	Synthetic	K	144°	$C_{25}H_{52}$	Interpolated		259°
$C_{16}H_{34}$	,,	K, F	158	$C_{26}H_{54}$	Paraffin F		268
$C_{17}H_{36}$	,,	K	171	$C_{27}H_{56}$	Synthetic K		277
$C_{18}H_{38}$	,,	K	184	$C_{28}H_{58}$	Paraffin F		286
$C_{19}H_{40}$	,,	K	196	$C_{29}H_{60}$	,,	F	295
$C_{20}H_{42}$	,,	K	208	$C_{30}H_{62}$	Synthetic F		304
$C_{21}H_{44}$	,,	K	219	$C_{31}H_{64}$	,,	K	312
$C_{22}H_{46}$	,, and paraffin	K, F	230	$C_{32}H_{66}$	,,	K	320
				$C_{33}H_{68}$	Interpolated		328
$C_{23}H_{48}$	,,	K	240	$C_{34}H_{70}$	Synthetic F		336
$C_{24}H_{50}$	,, and paraffin	K, F	250	$C_{35}H_{72}$	,,	K	344

K = Krafft. F = present communication.

The observed b. p. of our specimen of hexadecane on the thermometer used in this investigation was 278° at 764·8 mm.; correction for exposed stem raises this to 288·6°. Within the experimental error, this agrees with Krafft's determination, *viz.*, 287·5° at 760 mm.

Since the boiling point at 760 mm. recorded by Krafft for this hydrocarbon, and also those of $C_{17}H_{36}$, $C_{18}H_{38}$, and $C_{19}H_{40}$, all lie on a smooth curve connecting boiling points and carbon content, there can be no doubt that, as far as these hydrocarbons are concerned, Krafft's data at normal pressure were corrected for the exposed stem of the thermometer.

Our warmest thanks are due to Professor Sydney Young of Trinity College, Dublin, for the great assistance he has given us in considering and comparing our results with those of Krafft. In Krafft's communications to the *Berichte* there are many cases in which it is not possible to be certain whether the data recorded have or have not been corrected in the manner discussed in this communication.

THE UNIVERSITY, BRISTOL. [*Received, January 28th,* 1926.]

CLXXXV.—*The Monochloro-derivatives of* m-*Cresol.*

By GEORGE PHILIP GIBSON.

EXCEPT in the case of 6-chloro-*m*-cresol (Kalle and Co., D.R.-PP. 90,847 and 93,694; Friedländer's "Fortschritte," Vol. IV, 94) and 6-chloro-*m*-methoxybenzoic acid (Peratoner and Condorelli, *Gazzetta*, 1898, **28**, i, 214), little information is given in the literature regarding the monochloro-derivatives of *m*-cresol (Mazzura, *Gazzetta*, 1899, **29**, i, 380; 1900, **30**, ii, 84; Friedländer and Schenk, *Ber.*, 1914, **47**, 3040; Raschig, D.R.-P. 232,071, 1909; Biechele, *Annalen*, 1869, **151**, 115).

The author has studied the monochlorination of *m*-cresol, isolated the 2-, 4-, and 6-chloro-*m*-cresols (the first with difficulty), and converted them into the corresponding chloro-*m*-methoxybenzoic acids. The constitutions of these were determined by preparing the respective compounds from the corresponding 2-, 4-, and 6-nitro-*m*-cresols (Gibson, J., 1923, **123**, 1267) by successive methylation, reduction, substitution of chlorine for the amino-group, and oxidation of the resulting chloro-*m*-tolyl methyl ethers.

The reduction of 2-nitro-*m*-tolyl methyl ether by tin and hydrochloric acid produces an oily mixture of bases instead of the pure 3-methoxy-*o*-toluidine which is formed when iron and dilute acetic acid are used (Gibson, *loc. cit.*). The least volatile constituent of this mixture is a chloro-base, m. p. 47°. This is probably 5-chloro-3-methoxy-*o*-toluidine, since an isomeric base, m. p. 50°, was obtained by reducing 6-chloro-2-nitro-*m*-tolyl methyl ether.

EXPERIMENTAL.

Chlorination of m-*Cresol.*—A saturated solution of chlorine (1·1 mols.) in carbon tetrachloride (7·5 g. in 100 c.c.) was added gradually to a mechanically stirred solution of *m*-cresol in carbon tetrachloride. The solvent was then evaporated and the residue fractionally distilled. After five operations, 37% of the product boiled at 196—197° and 47% at 231—233°.

The fraction, b. p. 196—197°, was seeded at 0° with a crystal of 4-chloro-*m*-cresol obtained by the hydrolysis of 4-chloro-*m*-tolyl toluene-*p*-sulphonate. The crystals thus produced were separated from the residual oil, washed quickly with ice-cold light petroleum, and recrystallised from that solvent. The crystals obtained by seeding the residual oil, diluted with an equal volume of light petroleum (b. p. 50—60°), at −15° were similarly treated.

4-*Chloro*-m-*cresol* was thus obtained (29% of the fraction) in large, colourless prisms, m. p. 46°, b. p. 196° (Found: Cl, 24·8.

C_7H_7OCl requires Cl, 24·8%). The *methyl ether* is a colourless, pleasant-smelling liquid, b. p. 212·5°. The *acetate* has b. p. 122—123°/11 mm. The *benzoate* separates from alcohol in massive tablets containing alcohol, m. p. 31°, and from light petroleum in crystals, m. p. 40°. The *toluene*-p-*sulphonate*,

$$C_6H_3MeCl{\cdot}O{\cdot}SO_2{\cdot}C_6H_4Me,$$

crystallises from alcohol or acetone in large, six-sided prisms, m. p. 96°. It is sparingly soluble in alcohol or light petroleum.

The mixture of chloro-*m*-cresols obtained from the final petroleum mother-liquor (p. 1424) was converted almost quantitatively by treatment with sodium hydroxide solution and methyl sulphate into a mixture of ethers, b. p. 218—219°, which on oxidation with boiling dilute permanganate solution gave a theoretical yield of a mixture, m. p. 185—196°, of chloromethoxybenzoic acids. This mixture, systematically crystallised from chloroform, gave 42% of 4-chloro-*m*-methoxybenzoic acid, m. p. 211°. The final mother-liquors yielded a glue-like mass, which was dissolved in ether and fractionally extracted with 1% aqueous sodium hydroxide; the ethereal solution of the acid from each of these fractions was again extracted with an aqueous solution of the sodium salt of the next fraction. By repeated treatment of this kind, the mixture was completely separated into 2-chloro- and 4-chloro-*m*-methoxybenzoic acids.

2-*Chloro*-m-*cresol*, the presence of which in the crude chlorination product was thus established, was obtained by boiling its methyl ether (below) with hydriodic acid for 6 hours. The product was freed from the unchanged methyl ether with the aid of sodium hydroxide and distilled (b. p. about 194°); it then crystallised from light petroleum in massive, ill-defined, transparent crystals, m. p. 55—56°, having a pronounced phenolic odour and being very sparingly soluble in cold water. The *methyl* ether, prepared from 2-nitro-*m*-tolyl methyl ether (p. 1426), crystallised from light petroleum in massive prisms, m. p. 24·2°, b. p. 218·5° (Found: Cl, 22·7. C_8H_9OCl requires Cl, 22·7%).

6-*Chloro*-m-*cresol*.—A portion (49%) of the fraction of the crude chlorination product, b. p. 231—233°, solidified, and recrystallisation from light petroleum gave pure 6-chloro-*m*-cresol, m. p. 57° (Kalle and Co., *loc. cit.*, give 66°), b. p. 234° (Found: Cl, 24·9. Calc.: Cl, 24·8%).

The *methyl* ether boils at 213·5° and the *acetate* at 123—124°/11 mm. The *benzoate*, m. p. 86°, crystallises in thin, rectangular plates from alcohol, carbon tetrachloride, or light petroleum, and is not freely soluble in the latter two (Found: C, 68·1; H, 4·5. $C_{14}H_{11}O_2Cl$ requires C, 68·2; H, 4·4%). The *toluene*-p-*sulphonate*,

m. p. 98°, crystallises from alcohol and light petroleum, in both of which it is only slightly soluble, in plates and needles respectively.

The mother-liquors from the 6-chloro-*m*-cresol (p. 1425) gave, on evaporation, a solid of low melting point, which was treated with methyl sulphate and alkali; the resulting mixture of methyl ethers * gave, after repeated fractional distillation, 35% of 6-chloro-*m*-tolyl methyl ether (b. p. 213·5°) and about 21% of a liquid, b. p. 248—249°, which was probably a mixture of 2 : 6- and 4 : 6-dichloro-*m*-tolyl methyl ethers.

Reduction of 2-*Nitro*-m-*tolyl Methyl Ether* (compare Gibson, J., 1923, **123**, 1267; Hodgson and Beard, J., 1925, **127**, 498).—By the action of tin and hydrochloric acid on this ether a mixture (m. p. 27°) of 3-methoxy-*o*-toluidine and 5-chloro-3-methoxy-*o*-toluidine (about 10% of the product) is produced. The former is removed by fractional distillation in steam, and the residue, after being freed from a red impurity by distillation in a vacuum, separates from light petroleum in slender needles of *5-chloro-3-methoxy-o-toluidine*, m. p. 47°, b. p. 140—142°/11·5 mm., which are slightly soluble in light petroleum (Found: N, 8·1. $C_8H_{10}ONCl$ requires N, 8·2%).

The *acetyl* derivative, obtained by means of acetic anhydride containing a trace of sulphuric acid (Smith and Orton, J., 1908, **93**, 1250), crystallises from alcohol, acetone, or benzene in colourless needles, m. p. 170°. It is sparingly soluble in water, light petroleum, carbon tetrachloride, or benzene (Found: N, 6·5. $C_{10}H_{12}O_2NCl$ requires N, 6·6%).

2-*Chloro*-m-*tolyl Methyl Ether*.—The more volatile portion of the steam distillate (see above), consisting of 3-methoxy-*o*-toluidine with a small proportion of the chloro-base just described, is transformed into a mixture of chloro- and dichloro-*m*-tolyl methyl ethers by the Sandmeyer method. This product is distilled in steam, extracted from the distillate with ether, freed from any phenolic compounds by shaking with dilute aqueous alkali hydroxide, and repeatedly fractionally distilled. 2-Chloro-*m*-tolyl methyl ether (p. 1425) is thus obtained in a pure state (yield 54%, calculated on the nitro-compound used). The fractions of high boiling point, after distillation in a vacuum and recrystallisation from light petroleum, give 2 : 5-*dichloro*-m-*tolyl methyl ether* (yield 8·7%), which crystallises from light petroleum in slender

* Methylation in this type of compound overcomes the lowering of the boiling point due to the ortho Cl : OH grouping and the effect of a second chlorine atom in the molecule is then appreciable : 6-chloro-*m*-tolyl methyl ether boils at 213·5° and 4 : 6-dichloro-*m*-tolyl methyl ether at 249°, whereas the corresponding cresols boil at 234° and 232°, respectively.

prisms, m. p. 52°, b. p. 119—120°/12·5 mm., having the pleasant odour characteristic of these chloro-ethers (Found : OMe, 16·2; Cl, 37·0. $C_8H_8OCl_2$ requires OMe, 16·2; Cl, 37·1%).

6-*Chloro*-2-*nitro*-m-*tolyl methyl ether* is formed when 2-nitro-*m*-tolyl methyl ether is treated with chlorine at 160—170° until the gain in weight corresponds to 1 g.-atom. The dark reddish-brown product is repeatedly distilled (10 mm.) to free it from unchanged 2-nitro-ether (b. p. 120—130°), and the larger fraction (b. p. 140—145°), which solidifies, is fractionally crystallised from alcohol in order to remove some impurity, probably 4-chloro-2-nitro-*m*-tolyl methyl ether, which crystallises from the mother-liquors in tufts of very slender needles.

The 6-chloro-derivative (yield 55%) crystallises readily from alcohol, light petroleum, or carbon tetrachloride in large, pale yellow prisms, m. p. 112°. It is sparingly soluble in hot or cold water, alcohol, light petroleum, or carbon tetrachloride, but is fairly easily soluble in acetone, benzene, or chloroform (Found : Cl, 17·9. $C_8H_8O_3NCl$ requires Cl, 17·65%).

6-*Chloro*-3-*methoxy*-o-*toluidine*, prepared by reducing the preceding compound with iron borings and dilute acetic acid (compare p. 1424), crystallises from light petroleum, in which it is fairly easily soluble, in long needles, m. p. 50°, b. p. 145—146°/12 mm. (Found : N, 8·2. $C_8H_{10}ONCl$ requires N, 8·2%).

The *acetyl* derivative, m. p. 154°, crystallises readily from organic solvents, and is sparingly soluble in light petroleum, carbon tetrachloride, or benzene (Found : N, 6·3. $C_{10}H_{12}O_2NCl$ requires N, 6·6%).

When diazotised 6-chloro-3-methoxy-*o*-toluidine is treated with an alkaline solution of sodium stannite, and the resulting 6-chloro-*m*-tolyl methyl ether (b. p. 213—214°) oxidised with boiling dilute permanganate solution, 6-chloro-*m*-methoxybenzoic acid, m. p. 173·5°, is obtained (p. 1428).

Orientation of the 2-, 4-, *and* 6-*Chloro*-m-*cresols*.—The orientation of 2-chloro-*m*-cresol, by the preparation of its methyl ether from 2-nitro-*m*-cresol, has already been described (p. 1426). From the isomeric 4- and 6-nitro-*m*-cresols, the corresponding chloro-*m*-tolyl methyl ethers were prepared in a similar manner and oxidised to the corresponding chloro-*m*-methoxybenzoic acids. These compounds were identical respectively with those prepared by methylating the 4- and 6-chloro-*m*-cresols and oxidising the methyl ethers to the corresponding chloro-acids. These results are confirmed by the observed differences in the rates of oxidation of the methyl ethers to the acids; comparative experiments showed that the times required for the oxidation of equal weights (5 g.) of the

ethers were: 2-chloro-, 7·25 hours; 4-chloro-, 2·7 hours; and 6-chloro-, 6·7 hours.

2-*Chloro*-m-*methoxybenzoic acid*,* m. p. 160·5°, is almost insoluble in benzene, chloroform, carbon tetrachloride, or light petroleum (b. p. 60—80°) (Found: equiv., 186·9. Calc. for $C_8H_7O_3Cl$: equiv., 186·5). 4-*Chloro*-m-*methoxybenzoic acid*,* m. p. 211°, crystallises from 50% aqueous alcohol in slender prisms and from chloroform in plates (Found: equiv., 186·5). 6-Chloro-*m*-methoxybenzoic acid, m. p. 173·5° (Peratoner and Condorelli, *loc. cit.*, give 171°), is only sparingly soluble in benzene, light petroleum, or carbon tetrachloride, but dissolves freely in alcohol, acetone, or chloroform (Found: equiv., 187·6).

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UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, February 4th*, 1926.]

CLXXXVI.—*The Action of Thionyl Chloride on Hydroxyanthraquinones. Part II. Quinizarin.*

By ALBERT GREEN.

THE action of quinizarin on boiling thionyl chloride is different from that of alizarin (J., 1924, **125**, 1450). One hydroxyl group of quinizarin is replaced by a chlorine atom, which is reactive, and the product consists of deep red needles. In these and other properties the compound differs from the known monochloro-monohydroxyanthraquinones.

Slight loss of chlorine (1—2%) occurs when the compound is heated at 100°, or is boiled with acetic acid, for 1 hour. When a solution in concentrated sulphuric acid is heated on the boiling water-bath, the chlorine is eliminated as hydrogen chloride, and after 1 hour quinizarin is obtained in quantitative yield. The same product results from treatment with aqueous alkalis, and also by heating the *chloro*-compound under pressure with absolute methyl or ethyl alcohol or with acetic acid.

Oxidation with alkaline permanganate yields phthalic acid.

When a solution of the chloro-compound in absolute alcohol containing 3% of hydrogen chloride is heated, a product is obtained

* Since this paper was written, these acids have been prepared by Hodgson (this vol., p. 150).

which is isomeric with the known monoethyl ether of quinizarin (Liebermann and Jellinek, *Ber.*, 1888, **21**, 1168). This product is converted into quinizarin by heating it with concentrated sulphuric acid at 100° for an hour.

Treatment of the chloro-compound with boiling acetic anhydride, alone or with concentrated sulphuric acid, converts it into diacetyl derivatives of quinizarin. Efforts to isolate a monoacetyl derivative were fruitless, as in all cases some decomposition occurred with loss of chlorine. Similarly the products of methylation with diazomethane were not uniform and contained varying amounts of chlorine, although the analyses pointed to the presence of one methoxyl group only.

The chloro-compound condenses rapidly with boiling aniline and *p*-toluidine with loss of hydrogen chloride and production of *monoaminomonohydroxy*-compounds; longer treatment in presence of boric acid gives *diaminoanthraquinones*. These derivatives are respectively isomeric with the mono- and di-amino-compounds obtained by the condensation of quinizarin with aromatic amines, and the different colours of the solutions in concentrated sulphuric acid afford a means of distinguishing the isomerides.

While the replacement of one hydroxyl group of quinizarin by chlorine would be expected to give 1-chloro-4-hydroxyanthraquinone, it is obvious that the properties of the compound under consideration are not consonant with those of a chlorohydroxyanthraquinone in which the halogen is in one of the outer rings. 1-Chloro-4-hydroxyanthraquinone separates from alcohol in golden-yellow needles melting at 193°. It is unaffected by heating its solution in concentrated sulphuric acid for 1 hour at 100°, and is converted into quinizarin only when it is heated for several hours at 140° with sulphuric and boric acids (Eckert and Steiner, *Monatsh.*, 1914, **35**, 1145).

The replacement of a hydroxyl group by a chlorine atom by means of thionyl chloride connotes an acidic hydroxyl, and this is a well-known method of preparing the acid chlorides of carboxylic acids. Properties similar to those of an acid chloride are shown by this new derivative of quinizarin; such are its rapid condensation with amines, and the tendency of the chlorine atom to react with diazomethane. The interaction of what may be called "normal" chloroanthraquinones with amines is slow even in the presence of catalysts (compare, among others, Harrop, Norris, and Weizmann, J., 1909, **95**, 1313). Meyer and Sander (*Annalen*, 1912, **396**, 145), however, have shown that halogen-substituted anthrones, in which the halogen atom is attached to a *meso*-carbon atom, react readily with amines, giving aminoanthrones.

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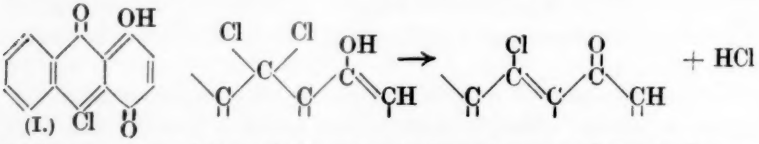
The only structure which appears to account adequately for the properties of the new compound is that of 10-*chloro*-1-*hydroxy*-4 : 9-*anthraquinone* (I). This formula *necessitates* an ortho-quinonoid grouping, and in this connexion the deep red colour of the compound is noteworthy, and is not found in "normal" monohydroxy-9 : 10-anthraquinones, which are yellow.

Probably 10-chloro-1-hydroxy-4 : 9-anthraquinone is formed from quinizarin in one of two ways. (1) Quinizarin may exist in a reactive ortho-quinonoid state in which the two hydroxyl groups are in the 1 : 10 positions instead of the 1 : 4 as usually formulated. α-Hydroxyl groups of hydroxyanthraquinones react with methylating and acylating agents much less rapidly than similar groups in β-positions. This fact and others have given rise to suggestions both of co-ordination between the hydrogen atoms of the α-hydroxyls and the neighbouring carboxyl oxygen atoms (Dimroth and Faust, *Ber.*, 1921, **54**, 3020; Sidgwick and Callow, J., 1924, **125**, 527), and also of isomeric structures in which the hydrogens of the α-hydroxyl groups are attached to the *meso*-oxygen atoms (Perkin, J., 1899, **75**, 453; Georgievics, *Monatsh.*, 1911, **32**, 329), to give ortho-quinonoid formulæ. There is, however, no recorded instance of a hydroxy-9 : 10-anthraquinone reacting in such an isomeric form.

(2) The reaction may occur in two stages. The first stage may be represented by the replacement of a carbonyl oxygen atom by two chlorine atoms—a reaction of this type occurs between benzaldehyde and thionyl chloride to give benzal chloride (Loth and Michaelis, *Ber.*, 1894, **27**, 2548). The second stage would then consist of the union of one of these chlorine atoms and the



hydrogen atom of the neighbouring hydroxyl group, giving hydrogen chloride and 10-chloro-1-hydroxy-4 : 9-anthraquinone. It is intended to test this theory of the mechanism of the reaction by an examination of the action of thionyl chloride on the ethers of quinizarin.

Both the above interpretations leave unexplained why only one of the carbonyl groups of quinizarin appears to take part in the reaction.

In the preparation of pure quinizarin for this investigation it was observed that the diacetyl derivative exists in two polymorphic forms with different melting points.

Experimental.

Quinizarin.—Pure diacetylquinizarin (see p. 1435) was heated with concentrated sulphuric acid (6 parts) at 100° for 30 minutes, and the solution was then stirred into cold water. After boiling for 10 minutes, the mixture was filtered, the quinizarin washed with boiling water until free from acid, and dried at 100°. It assumed a dark metallic lustre at 183° and melted at 197—198°.

10-*Chloro*-1-*hydroxy*-4 : 9-*anthraquinone.*—When 30 g. of quinizarin were boiled with 120 c.c. of recently distilled thionyl chloride, solution occurred rapidly with evolution of sulphur dioxide and hydrogen chloride. After 8—30 hours, the deep red liquid was concentrated to half bulk. On cooling in a dry atmosphere, it deposited dark red, fine needles (26 g.), m. p. 225—226° (even after recrystallisation from methyl or ethyl alcohol or benzene); a further 4 g. were obtained by concentrating the filtrate. The product was washed free from thionyl chloride with dry benzene and ether and dried in a vacuum over fused calcium chloride and soda lime (Found: C, 65·0; H, 2·8; Cl, 13·7; *M*, cryoscopic in naphthalene, 265, 260. $C_{14}H_7O_3Cl$ requires C, 65·0; H, 2·7; Cl, 13·7%; *M*, 258·5). It gave a bright red colour with alcoholic ferric chloride and when warmed with pyridine formed a dirty brown solution which slowly deposited a black, apparently amorphous powder.

A mixture of 40 c.c. of 10% aqueous potassium hydroxide, 2 g. of the quinone, and 100 c.c. of 10% potassium permanganate solution was boiled for 2 hours, and the excess of permanganate destroyed by alcohol; from the colourless acidified filtrate ether extracted 0·8 g. of impure phthalic acid (identified in the form of the anhydride, from which fluorescein was prepared).

Conversion into quinizarin. (1) *By sulphuric acid.* A solution (reddish-purple) of 0·86 g. of 10-chloro-1-hydroxy-4 : 9-anthraquinone in 20 c.c. of concentrated sulphuric acid was heated on a boiling water-bath for 1 hour and then poured into water, the suspension boiled, and the light red precipitate (0·79 g., theoretical) collected and dried (Found: C, 69·8; H, 3·3. Calc.; C, 70·0; H, 3·3%). It melted at 197° alone and when mixed with pure quinizarin, and when acetylated in pyridine gave a diacetyl derivative in prisms, m. p. 206—208°.

(2) *By acetic acid.* A mixture of 0·9 g. of the quinone and 2 c.c. of acetic acid was heated, with or without 0·3 g. of freshly-fused potassium acetate, in a sealed tube for 3 hours at 180°. The product, on recrystallisation from 20 c.c. of boiling acetic acid (bone charcoal), gave 0·3—0·4 g. of red needles which, alone or

mixed with pure quinizarin, melted at 197° (Found : C, 69·8; H, 3·4%).

(3) *By methyl alcohol.* When 0·85 g. of the quinone was heated in a sealed tube at 200° for 2 hours with 2 c.c. of absolute methyl alcohol, and the product recrystallised from methyl alcohol (bone charcoal), 0·4 g. of quinizarin, m. p. 196—197°, was obtained (Found : C, 70·0; H, 3·4%).

(4) *By ethyl alcohol.* When the experiment was repeated with absolute ethyl alcohol, 0·3 g. of quinizarin was obtained (Found : C, 69·7; H, 3·3%).

(5) *By sodium or potassium hydroxide.* A paste of the quinone (3 g.) and an excess of concentrated aqueous sodium or potassium hydroxide was boiled with water for 5 minutes and stirred into an excess of boiling dilute hydrochloric acid. The reddish-brown solid (2·5 g.) produced crystallised from acetic acid in red needles of quinizarin, m. p. 195—197° (alone and mixed) (Found : C, 69·7; H, 3·3%), which was converted into its diacetyl derivative, m. p. 206—208°.

Acetylation. (1) *Acetic anhydride alone.* 10-Chloro-1-hydroxy-4 : 9-anthraquinone (4 g.) was boiled with 40 c.c. of acetic anhydride until fumes of hydrogen chloride (due to decomposition, by atmospheric moisture at the top of the condenser, of acetyl chloride produced in the reaction) were no longer observed (4 hours). The original dark red colour became dark green, and from the filtered, cooled solution small, olive-green crystals (4·2 g.), m. p. 204°, separated. These were repeatedly crystallised from acetic anhydride (bone charcoal) and finally twice from pyridine; the characteristic yellow prisms of diacetylquinizarin were then obtained which, alone or mixed with an authentic specimen, melted at 207—208°. A quantitative experiment showed that the substance did not contain chlorine [Found : C, 66·7; H, 3·6; CH_3·CO, 26·7; *M*, in freezing naphthalene, 310, 315. Calc. for $C_{14}H_6O_4(CO\cdot CH_3)_2$: C, 66·7; H, 3·7; CH_3·CO, 26·7%; *M*, 324].

Hydrolysis of this acetyl derivative by an alcoholic solution of sulphuric acid yielded quinizarin, m. p. 198° (Found : C, 69·9; H, 3·3%).

(2) *Acetic anhydride and sulphuric acid.* When 2·2 g. of 10-chloro-1-hydroxy-4 : 9-anthraquinone were heated to boiling with 10 c.c. of acetic anhydride containing 2 drops of concentrated sulphuric acid, the red solution rapidly became yellow-green. The filtered solution slowly deposited 1·4 g. of very fine, pale yellow rods identical with those obtained by acetylating quinizarin under similar conditions (see under). The product of one recrystallisation from acetic anhydride containing sulphuric acid changed colour from yellow to light orange at about 120° and melted at 200—201°

(Found: C, 66·5; H, 3·8; $CH_3{\cdot}CO$, 26·6%). This diacetyl derivative separated from pyridine in small, yellow prisms, m. p. 207—208°.

Numerous experiments were carried out with a view to acetylating the single hydroxyl group. The chloro-compound was heated with acetyl chloride and potassium acetate under ordinary pressure, in benzene solution, and in sealed tubes at 90—100°. The products, however, were mixtures containing in some cases as little as 4% of chlorine. Attempted acetylations in pyridine with one molecular proportion of acetic anhydride yielded black amorphous products which would not crystallise and in which the chlorine content also varied.

Methylation of 10-*chloro*-1-*hydroxy*-4 : 9-*anthraquinone*. Since methylation in alkaline media was impossible, diazomethane was used. In every experiment chlorine was lost (4% in one experiment), and the products were not uniform. Nevertheless analyses clearly indicated the presence of one hydroxyl group.

In a typical experiment a suspension of 1·0 g. of the finely powdered dry compound in 30 c.c. of absolute ether at 5° was treated with an excess of diazomethane (from 2 g. of nitrosomethylurethane and 6 c.c. of 70% aqueous potassium hydroxide) in 60 c.c. of dry ether during ½ hour. Stirring was continued for 3 hours, and the red product (1 g.) collected after 12 hours. After darkening at about 190°, it melted to a black paste between 270° and 280° (Found: Cl, 12·1; OMe, 11·1. $C_{14}H_6O_2{\cdot}OMe$ requires Cl, 13·0; OMe, 11·4%).

Condensations with amines. (1) *Anilino-derivative*, $C_{14}H_7O_3{\cdot}NH{\cdot}C_6H_5$.

A solution of 1·5 g. of 10-chloro-1-hydroxy-4 : 9-anthraquinone in 8 c.c. of freshly distilled aniline was boiled for 5 minutes, the red colour changing to brown. The hot solution was stirred into an excess of dilute hydrochloric acid and boiled. The black precipitate was filtered off hot, washed free from acid and dried (1·9 g.). It separated from tetrachloroethane in black, microscopic crystals after the addition of a little ether. The product, which contained no chlorine, formed a paste at 272—274° and decomposed at 290°. It dissolved in concentrated sulphuric acid with a deep amethyst colour and in boiling sodium hydroxide to a very pale purple solution (Found: N, 4·3. $C_{20}H_{13}O_3N$ requires N, 4·4%).

(2) *Dianilino-derivative*, $C_{14}H_6O_2(NH{\cdot}C_6H_5)_2$. A mixture of 1 g. of the chloro-compound, 0·5 g. of boric acid (dried at 120° for 4 hours), and 10 c.c. of freshly-distilled aniline was boiled for 6 hours, the purple colour becoming dark brown. It was stirred while hot into an excess of dilute hydrochloric acid, and the pre-

cipitate treated as in the previous experiment. The product consisted of black crystals (1·6 g.) which did not melt below 310°. It gave a golden-brown solution in concentrated sulphuric acid, but was insoluble in hot aqueous caustic soda (Found : N, 7·2. $C_{26}H_{18}O_2N_2$ requires N, 7·2%).

The dianilino-derivative from quinizarin, prepared similarly, formed blue-black crystals from tetrachloroethane. These dissolved in sulphuric acid to a blue-black solution and were insoluble in boiling caustic soda solution (Found : N, 7·1%).

(3) *Mono*-p-*toluidino-derivative*, $C_{14}H_7O_3{\cdot}NH{\cdot}C_6H_4Me$. This was prepared in a similar manner to the monoanilino-derivative. The product, which was free from chlorine (Carius), crystallised from acetic acid in microscopic, very dark brown needles which softened at 280° and showed no further change up to 310°. Its solution in sulphuric acid was amethyst and in caustic soda light purple (Found : N, 4·1. $C_{21}H_{15}O_3N$ requires N, 4·3%).

The mono-*p*-toluidino-derivative * from quinizarin melted at 190—192°, and dissolved in concentrated sulphuric acid with a brilliant green colour (Found : N, 4·2%).

(4) *Di*-p-*toluidino-derivative*, $C_{14}H_6O_2(NH{\cdot}C_6H_4Me)_2$. This was prepared similarly to (2) above, and crystallised from alcohol in bluish-black, microscopic needles which decomposed at 305° with previous sintering. The solution in sulphuric acid was dark honey-coloured (Found : N, 6·7. $C_{28}H_{22}O_2N$ requires N, 6·7%).

The isomeric compound prepared from quinizarin gave a blue-black solution in concentrated sulphuric acid (Found : N, 6·8%).

10-*Ethoxy*-1-*hydroxy*-4 : 9-*anthraquinone*.—10-Chloro-1-hydroxy-4 : 9-anthraquinone (2·5 g.) was boiled with absolute ethyl alcohol (200 g.) containing 3% of dry hydrogen chloride for 3½ hours, the red solution becoming dark green and fluorescent. From the filtered, concentrated, cooled solution clusters of reddish-brown needles separated (2·1 g.), m. p. 135°, after recrystallisation from ethyl alcohol (Found : C, 71·3; H, 4·3; OEt, 16·3. $C_{14}H_7O_3{\cdot}OEt$ requires C, 71·6; H, 4·5; OEt, 16·9%).

This ether was very soluble in cold benzene and less soluble in cold ethyl alcohol. In concentrated sulphuric acid, its solution was similar to that given by quinizarin. When this solution was heated at 100° for 1 hour and then stirred into water, quinizarin (m. p. 195—197°) was obtained in quantitative yield (Found : C, 70·0; H, 3·4%).

1-*Chloro*-4-*acetoxyanthraquinone*.—Commercial 1-chloro-4-hydroxyanthraquinone † was boiled with an excess of acetic anhydride

* Kindly presented by the British Alizarine Co., Ltd., Manchester.

† Kindly presented by the Scottish Dyes, Ltd., Carlisle.

and a few drops of pyridine for ½ hour. The crude acetyl derivative was repeatedly crystallised from pyridine containing a little anhydride, until the melting point remained constant at 176—177°, the pure 1-*chloro*-4-*acetoxyanthraquinone* forming fine, pale primrose needles (Found: Cl, 11·8; CH_3·CO, 14·4. $C_{14}H_6O_3Cl$·CO·CH_3 requires Cl, 11·8; CH_3·CO, 14·3%).

1-*Chloro*-4-*hydroxyanthraquinone*.—The pure acetyl derivative (2 g.) was hydrolysed by boiling for 2 hours with 140 c.c. of absolute alcohol containing 3 c.c. of concentrated sulphuric acid. On cooling, the hydroxy-compound separated in golden-yellow needles, m. p. 192—193°, unchanged by further recrystallisation (Found: Cl, 13·8. Calc. for $C_{14}H_7O_3Cl$: Cl, 13·7%). The alcoholic solution of 1-chloro-4-hydroxyanthraquinone gave a pale red colour with ferric chloride.

Treatment of 1-*Chloro*-4-*hydroxyanthraquinone with Sulphuric Acid*.—A solution of 3 g. in 50 c.c. of concentrated sulphuric acid was heated at 100° for 1 hour. The hot liquid was then stirred into 200 c.c. of cold water, the mixture boiled for 10 minutes, and the yellow product filtered off, washed with boiling water until acid-free, and dried at 100° (2·8 g.). The substance melted at 192°, alone and when mixed with an authentic specimen of 1-chloro-4-hydroxyanthraquinone (Found: Cl, 13·7%).

Diacetylquinizarin.—Liebermann and Giesel (*Ber.*, 1875, **8**, 1648) describe diacetylquinizarin as "gelbe Saulchen" melting at 200°.

Quinizarin supplied by the British Dyestuffs Corporation, Ltd., was acetylated by boiling for 15 minutes with acetic anhydride containing a few drops of concentrated sulphuric acid. The product on purification was obtained in two polymorphic forms:

Form A. (1) Small, twinned, six-sided, yellow prisms from quickly chilled solutions in hot pyridine [Found: C, 66·6; H, 3·7; CH_3·CO, 26·8; *M*, cryoscopic in naphthalene, 325.

$$C_{14}H_6O_4(CO{\cdot}CH_3)_2$$

requires C, 66·7; H, 3·7; CH_3·CO, 26·7%; *M*, 324]. (2) Long, flat, six-sided, yellow plates by recrystallisation from acetic anhydride alone (Found: C, 66·4; H, 3·6; CH_3·CO, 26·6%; *M*, 330). (3) Very thin, pale yellow needles from alcohol (Found: C, 66·7; H, 3·6; CH_3·CO, 26·9%; *M*, 26·9). All three forms melted at 207—208°.

Form B. Sheaves of yellow needles or fine rods, which became light orange at about 120° and melted at 200—201° (Found: C, 66·6; H, 3·6; CH_3·CO, 26·2%; *M*, 320). This form was converted into A by recrystallisation from pyridine, acetic anhydride, or alcohol, and hot solutions of *A* in acetic anhydride containing a few drops of sulphuric acid always deposited crystals of B only.

Solubility Determinations.—The two forms of the diacetyl derivative have identical solubilities in benzene and in chloroform at 25°. This may be accounted for by the long time required for saturation. Benzene, for example, was still unsaturated with respect to A after 15 hours' shaking at 25°.

In Table I the figures represent g. of solute per 100 g. of solution.

TABLE I.

Substance.	Benzene.				Chloroform.			
	20 hrs.	30 hrs.	55 hrs.	Mean.	40 hrs.	55 hrs.	65 hrs.	Mean.
A 1	0·693	0·699	0·694	0·70	5·01	5·05	5·01	5·0
A 2	0·698	—	0·699	0·70	—	5·00	—	5·0
A 3	0·698	—	0·697	0·70	—	—	—	—
B	0·694	0·700	0·699	0·70	—	5·03	5·03	5·0
A + B	—	—	0·701	0·70	—	—	—	—

Benzene was freed from thiophen, washed, dried over calcium chloride, fractionated, and distilled from sodium before use. A uniform sample was used throughout.

"Pure" chloroform was washed with alkali, acid, and water, dried over calcium chloride, and twice distilled, and a constant boiling fraction was used.

The sealed solubility tubes were attached to a large paddle stirrer, which was rotated continuously in an electrically heated thermostat (25° ± 0·025°). Samples were taken, after settling, in 50 c.c. pipettes fitted with short removable glass tubes plugged with cotton wool.

The weighing bottles were dried to constant weight at 90°. Constant weighings (± 0·0002 g.) were obtained by allowing the bottles, when removed from the oven, to stand in a desiccator over sulphuric acid for precisely 30 minutes, and by taking the final readings after the bottles had been on the balance for 2 minutes.

Cryoscopic Measurements.—In applying the test suggested by Sidgwick (J., 1915, **107**, 672) for distinguishing between polymorphic, isomeric and tautomeric substances, solvents with low freezing points such as benzene and nitrobenzene could not be used, owing to the small solubilities of the acetyl derivatives in them and also to the long time required for saturation. Naphthalene was used and saturated solutions were obtained in a few minutes at a degree or two above its freezing point. Table II shows the results of these experiments.

TABLE II.

Substance.	Weight of solvent (g.).	Maximum depression.
A 1 alone	7·785	1·95°
After addition of B	,,	1·90
B alone	7·780	1·95
After addition of A 1	,,	1·92

The determinations were carried out in a small Beckmann apparatus fitted with a thermometer graduated in tenths of a degree. This could be read to the nearest fortieth of a degree with ease.

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THE EDWARD DAVIES LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. [*Received, February 4th*, 1926.]

CLXXXVII.—*The Heat of Combustion of Salicylic Acid. (A Reply to E. Berner.)*

By PIETER EDUARD VERKADE and JAN COOPS.

DURING the last few years investigations on thermochemical standard substances, carried out in various places, have led to the adoption of benzoic acid, by international consent, as the exclusive standard substance to be used in determinations of heats of combustion. The value 6324 cal.$_{15°}$ per g. (air) (v = constant), *i.e.*, 6319 cal.$_{15°}$ per g. (vac.), has been accepted for the heat of combustion of this substance. At the same time, it was decided that, for scientific work, use should always be made of benzoic acid furnished for this purpose by the Bureau of Standards, Washington (*Compt. rend. de la troisième Conférence Internationale de la Chimie*, Lyons, 1922, p. 54; compare Verkade, *Chem. Weekblad*, 1922, **19**, 389; 1924, **21**, 13).

For some time we have tried to make it clear that this regulation is not quite sufficient. The heat capacity of a calorimetric system, found exclusively by means of this benzoic acid, is always somewhat uncertain; accidental errors, caused by contamination of the standard preparation, during packing or in the course of time, can be brought to light only with difficulty, if at all. We therefore emphasised strongly the desirability of introducing one or more further thermochemical standard substances (which, if so desired, could be considered as *secondary* standards) and, on the grounds of an extensive research, recommended salicylic acid for this purpose (Verkade and Coops, *Rec. trav. chim.*, 1924, **43**, 561).

The heats of combustion of various samples of salicylic acid were determined with the following results, valid for an isothermal reaction at 19·5°, at constant volume and on the assumption that the above-mentioned heat of combustion of benzoic acid holds for the same temperature (compare Verkade, *Rec. trav. chim.*, 1925, **44**, 799).

Sample.	Heat of combustion per g. (air).
Poulenc (" Standard pour calorimétrie ")	5241·4 cal.$_{15°}$
Merck (" Präparat von bestimmter Verbrennungswärme ")	5241·7 ,,
Merck (crystallised from ether)	5241·3 ,,
Von Heyden (" Acid. Salicylicum recrystallis. puriss.")...	5242·8 ,,
Kahlbaum (" für kalorimetrische Bestimmungen ")	5242·6 ,,
Commercial (" Acid. Salicyl. praec. pulv.") (crystallised twice from water and once from chloroform)	5242·3 ,,

Thus a number of the purest samples obtainable commercially, most of them supplied especially for calorimetric purposes, furnished values for the heat of combustion which agreed within the error of observation. The heat of combustion of one of these samples remained unchanged when the substance was recrystallised from ether. A technical preparation taken from the Dutch market gave the same heat of combustion after purification. On the basis of these facts, we considered ourselves completely justified in regarding the mean of all our measurements as the heat of combustion of *pure* salicylic acid. This heat of combustion is 5241·9 cal.$_{15°}$ per g. (air) (v = constant; 19·5°), *i.e.*, 5238·3 cal.$_{15°}$ per g. (vac.). The ratio of the heats of combustion of benzoic acid and salicylic acid is then 6324/5241·9 = 1·2064 (air).

Our work has recently been criticised by Berner (J., 1925, **127**, 2747). Let it be said that this author shares our views regarding the desirability of introducing a second or secondary thermochemical standard substance and admits the particular suitability of salicylic acid for this purpose. However, we are said not to have taken the necessary care to ensure the greatest possible purity of our samples of salicylic acid and, on that account, to have found too high a heat of combustion; according to Berner, the heat of combustion of salicylic acid is only 5237·4 cal.$_{15°}$ per g. (air) (v = constant; about 18°), *i.e.*, 5233·8 cal.$_{15°}$ per g. (vac.). The ratio of the heats of combustion of benzoic and salicylic acids should then be 6324/5237·4 = 1·2075 (air).

Berner seems to have overlooked the fact that the heat of combustion found by us was already confirmed from two sides :

1. Roth burnt salicylic acid in the micro-bomb and microcalorimeter which he has constructed and found 5241·5 cal.$_{15°}$ per g. (air) for the heat of combustion, which deviates from our value by only — 0·08 part per 1000 parts (*Z. Elektrochem.*, 1924, **30**, 607). Also, Roth has investigated salicylic acid in a bomb of normal dimensions and the well-known calorimetric apparatus of Stohmann-Hugershoff (*Naturwiss.*, 1924, **12**, 652); it is, however, simply stated there that the heat of combustion found agreed exactly with ours. We have learned some details from a private

communication, which, by kind permission of Prof. Roth, we are able to publish. Various samples of salicylic acid from von Heyden gave concordant heats of combustion; an arbitrarily chosen commercial sample was purified by crystallisation from alcohol and after careful drying gave the same heat of combustion, which did not alter when the sample was recrystallised from alcohol and from water. The mean value of all these measurements was 5241·3 cal.$_{15°}$ per g. (air) (v = constant; 18·3°); the deviation from our value amounted therefore to only − 0·11 part per 1000 parts.

2. Swientoslawski (*Bull. Soc. chim.*, 1925, **37**, 84) found 5242·4 cal.$_{15°}$ per g. (air) for the heat of combustion of a commercial sample of salicylic acid, which was crystallised several times from water. This value deviates from ours only by about + 0·10 part per 1000 parts. Details of these measurements were not published.

These facts made it *a priori* scarcely possible for us to believe in the accuracy of Berner's results. It was improbable that the numerous preparations used by Verkade and Coops, by Roth, and by Swientoslawski—notwithstanding their different origins and different modes of purification—should all show a large surplus of exactly the same magnitude in the heat of combustion.

Nevertheless, we considered that our work ought to be controlled. In the first place, we again burnt one of the preparations which we had used previously (namely, that of Merck), making use of another bomb and of a calorimetric apparatus of considerably greater heat-capacity than that used previously. Secondly, we carefully subjected the previously used sample from von Heyden to various purification processes and measured the heat of combustion after each purification in the same apparatus. The results of these measurements are in the following table.

Material.	Heat of combustion per g. (air). (v = constant; 19·5°).
Merck	5242·3
Von Heyden (crystallised twice from water, once from chloroform)	5241·4
Von Heyden (further crystallised from ether)	5241·5
,, (further crystallised from benzene)	5241·9

Thus we see that continued purification of von Heyden's salicylic acid brings about no change in the heat of combustion. The mean value of our 15 experiments with this acid in its various stages of purification is 5241·7 cal.$_{15°}$ per g. (air) (v = constant; 19·5°). This new value for the heat of combustion of salicylic acid deviates from the one we found previously by only − 0·04 part per 1000 parts. For the ratio of the heats of combustion

of benzoic and salicylic acids we now obtain the value 6324/5241·7 = 1·2065 (air), which is practically identical with that found previously. We have no reason to doubt the correctness of this value, as the ratios of the heats of combustion of benzoic acid and naphthalene, and of benzoic acid and cane-sugar, obtained by us at about the same time (Verkade, Coops, and Hartman, *Rec. trav. chim.*, 1922, **41**, 241; Verkade and Coops, *ibid.*, 1923, **42**, 205) are in full agreement with those obtained recently in very careful work by other authors (Dickinson, *Bull. Bureau of Standards*, 1914, **11**, 243; Swientoslawski and Starczewska, *Bull. Soc. chim.*, 1922, (4), **31**, 654; Schläpfer and Fioroni, *Helv. Chim. Acta*, 1923, **6**, 713), and at present generally accepted.

Hence we reach the conclusion that Berner found a value for the heat of combustion of salicylic acid which is too low, and that his results are subject to an error of about 0·8 part per 1000 parts. We are not able to indicate the cause of this error. At our request, Mr. Berner had the kindness to provide us with small quantities of two samples of salicylic acid which he had used in his research. These were the samples designated by Berner as 571II (Merck's acid, crystallised twice from water and once from chloroform) and 572IV (Kahlbaum D.A.B.5, subjected to sublimation in a vacuum and to several crystallisations from water, chloroform, and benzene). These samples yielded in our hands values for the heats of combustion of 5241·6 and 5241·9 $cal._{15°}$ per g. (air), respectively. These values are practically identical with those obtained by us for our own specimens. Berner as well as ourselves used benzoic acid from the Bureau of Standards, Washington (Standard Sample 39*b*) in the calibration of the calorimetric apparatus.

As far as we know, Berner has not burnt standard samples of naphthalene and cane-sugar in his apparatus. The possibility therefore exists that, on burning these substances, this author may find, for the ratios mentioned above, values different from those now generally accepted as correct. In this case, the low heat of combustion of salicylic acid found by this author would be due to a slight error in the determination of the heat capacity of his apparatus.

Experimental.

The following alterations have been made in the calorimetric apparatus used for our previous measurements of the heat of combustion of salicylic acid (Verkade and Coops, *loc. cit.*) and described in detail in our first communication on heats of combustion of organic compounds (Verkade, Coops, and Hartman, (*Rec. trav. chim.*, 1922, **41**, 241).

We now used a silver calorimeter can of greater capacity than that used formerly, so that the quantity of water could be increased to about 2600 g., as well as a bomb of rustless V_2A steel, supplied by the firm of Hugershoff, Leipzig, and especially suited, in our experience, for work of high precision.

For the method of carrying out the measurements reference may be made to the literature cited above.

Heat Capacity of the Calorimetric Apparatus.—This was determined by burning three samples of benzoic acid, namely, two standard preparations (Standard Samples 39*a* and 39*b*) from the Bureau of Standards, Washington, and one prepared by ourselves, which had already served for earlier work. At an oxygen pressure of 35 atms. the heat capacity was 3051·2 cal.$_{15°}$ at a temperature of 19·5°. It seems unnecessary for us to give full details of our measurements, but we give a statement of results :

Sample.	Heat capacity.	Sample.	Heat capacity.
39*a*	3050·0	39*b*	3050·0
,,	3049·6	,,	3051·4
,,	3051·4	,,	3051·8
,,	3051·6	,,	3052·4
,,	3051·3	Rotterdam	3050·9
,,	3050·2	,,	3052·3
,,	3051·2	,,	3051·8
		,,	3052·5

For some observations regarding the heat capacity found in this way (*i.e.*, by the combustion of a standard substance), reference may be made to a paper by one of us (Verkade, *Rec. trav. chim.*, 1925, **44**, 799).

We were able to verify this heat capacity repeatedly by indirect methods, namely, by burning substances which we had already burnt before introducing the above-mentioned alterations in the calorimetric apparatus. Completely concordant results were obtained in both cases. Also (*e.g.*, in the case of *n*-butyl alcohol), we could obtain with our new apparatus complete concordance with the extremely accurate thermochemical work of Richards (compare Verkade and Coops, *Rec. trav. chim.*, 1926, in course of publication).

Salicylic Acid Preparations.—Von Heyden's " Acidum Salicylicum recrystallis. puriss " (used in our previous measurements) was crystallised twice from water. After drying in the air, it was very finely powdered and warmed to about 100° for 4 hours; during the heating it was again finely powdered several times. We have shown already (*Rec. trav. chim.*, 1924, **43**, 575) that salicylic acid can be heated for 20 hours at about 115° without undergoing even the slightest decomposition. This heating is necessary, since it has

been shown recently (*e.g.*, Cohen, Verkade, Saburo Miyake, Coops, and van der Hoeve, *Versl. Kon. Akad. Wetensch. Amsterdam*, 1926, **35**, 48) that on crystallisation from water, salicylic acid may occlude several parts of water per thousand, which is not removed even by very long drying in a vacuum over phosphorus pentoxide. However, this occluded water can be removed for the most part in the way described above, as was proved by determinations of the heat of combustion carried out expressly for this purpose. The sample obtained in this way was then recrystallised from dry chloroform (sample II); the last traces of water in the crystals were removed by distilling off a part of the solvent from the boiling solution, the water then passing over with the solvent. After a part of this sample had been burnt, the remainder was crystallised from dry ether (sample III) and finally from dry benzene (sample IV). All three samples were finely powdered and dried for several days in a vacuum over phosphorus pentoxide.

Merck's salicylic acid (" Präparat von bestimmter Verbrennungswärme) and Berner's samples 571II and 572IV were finely powdered and dried in the same way without other treatment.

Heat of Combustion of the Salicylic Acid Preparations.—On account of a small difference in the composition of the products of combustion of benzoic and salicylic acids, a correction of +0·1 cal.$_{15°}$ must be introduced in the above-mentioned heat capacity in combustions of the latter acid (compare *Rec. trav. chim.*, 1924, **43**, 566). We shall give no details of the measurements. We found the following values for the heat of combustion of salicylic acid per g. (air) (v = constant; 19·5°).

Sample.	Heat of combustion.	Mean.
Merck	5242·4, 5242·7, 5240·7, 5242·4, 5243·2	5242·3
II	5241·5, 5241·8, 5242·2, 5240·0, 5241·6	5241·4
III	5242·5, 5242·5, 5240·4, 5241·5, 5240·8	5241·5
IV	5242·6, 5240·8, 5241·6, 5241·7, 5242·9	5241·9
571 II	5241·6, 5241·5, 5241·7	5241·6
572 IV	5241·2, 5240·1, 5244·5	5241·9

Summary.

Our previous determinations of the heat of combustion of salicylic acid have been submitted to a control. The heat of combustion of this compound was found to be 5241·7 cal.$_{15°}$ per g. (air) (v = constant; 19·5°), a value practically identical with that found previously. Hence the heat of combustion found by Berner, namely, 5237·4 cal.$_{15°}$ per g. (air) (v = constant; about 18°), is too low.

This investigation was carried out with the aid of a grant from

the " Hoogewerff Fonds " and we take this opportunity of expressing our thanks to the Advisory Board of this Fund for the support we have received.

LABORATORIUM DER NEDERLANDSCHE HANDELS-HOOGESCHOOL, ROTTERDAM. [*Received, February 27th*, 1926.]

CLXXXVIII.—As-*Chlorotetrahydroarsinoline and Some Quaternary Arsonium Compounds.*

By ELWYN ROBERTS, EUSTACE EBENEZER TURNER, and (in part) FRANK WARD BURY.

As-METHYLTETRAHYDROARSINOLINE (Burrows and Turner, J., 1921, **119**, 426) readily forms a *dichloride*, which, when heated, is smoothly decomposed to give As-*chlorotetrahydroarsinoline*, the first simple cyclic chloroarsine of this series to be prepared.

Attempts to prepare arsinolines and arsindoles (or the corresponding intermediate compounds) are described in this paper.

The alternation in the physical properties of a series of benzene derivatives having normal side-chains is a subject of considerable interest. The following table shows that there is a marked alternation in the melting points of the first five members of the series of methiodides of the general formula $Ph\cdot[CH_2]_x\cdot AsMe_3I$.

$Ph\cdot AsMe_3I$	252°	$Ph\cdot[CH_2]_3\cdot AsMe_3I$	144°
$Ph\cdot CH_2\cdot AsMe_3I$	194—195	$Ph\cdot[CH_2]_4\cdot AsMe_3I$	150—151
$Ph\cdot[CH_2]_2\cdot AsMe_3I$	203—204*		

* Previously given (Turner and Bury, J., 1923, **123**, 2489) as 200°.

There is also a marked difference in the ease with which the five arsines of the type $Ph\cdot[CH_2]_x\cdot AsMe_2$ are prepared by the interaction of the appropriate Grignard reagent and dimethyliodoarsine. The respective percentage yields of phenyl-, phenylpropyl-, phenylbutyl-, phenylethyl-, and benzyl-dimethylarsine were 80, 65, 45, 45 (97*), and 20. We regard a low yield as being due to a high tendency, on the part of the arsine, to undergo oxidation, and conversely; we have, however, not conducted quantitative measurements on the subject.

[With F. W. BURY.] In view of the success achieved by Rosenheim and Plato (*Ber.*, 1925, **58**, 2000) and by Mills and Raper (J., 1925, **127**, 2479), experiments on the resolution of arsenic compounds in progress in this laboratory have been discontinued. Two asymmetric types were under examination; it has been found

* Preparation carried out in an inert atmosphere (Turner and Bury, *loc. cit.*).

impossible to resolve cyclo*hexylphenylbenzylmethylarsonium* d-α-*bromocamphor-π-sulphonate* and the *phenylbenzylarsinates* of *strychnine* and l-*menthylamine*. One or two compounds prepared incidentally are, however, now described.

EXPERIMENTAL.

γ-Phenylpropyldimethylarsine.—The dimethyliodoarsine required for this preparation (Burrows and Turner, *loc. cit.*) is most conveniently obtained by passing sulphur dioxide into a solution containing 225 g. of cacodylic acid, 450 g. of potassium iodide, 150 g. of concentrated sulphuric acid, and 1850 c.c. of water. *γ-Phenylpropyldimethylethylarsonium iodide* is formed fairly readily from the arsine and methyl iodide, and separates from alcohol–ether in colourless leaflets, m. p. 118° (Found: I, 33·3. $C_{13}H_{22}IAs$ requires I, 33·4%).

γ-Phenylpropylmethylchloroarsine was heated at 200° in a current of dry carbon dioxide, but although it underwent considerable apparent change, no hydrogen chloride was evolved. This is in interesting contrast to the ease with which *o*-phenoxyphenyldichloroarsine passes into 10-chlorophenoxarsine (Roberts and Turner, J., 1925, **127**, 2004).

Derivatives of As-*Methyltetrahydroarsindole.*—The methiodide melts at 239—240°, not at 235°, as previously recorded. The *ethiodide* is less readily formed than the methiodide, and separates from ether–alcohol in colourless prisms, m. p. 185—186° (Found: I, 34·8. $C_{12}H_{18}IAs$ requires I, 34·9%). The *benzobromide* is formed as a glassy mass when the components are warmed together, and is difficult to purify. It crystallises from ether–alcohol in colourless prisms, m. p. 210—211° (Found: Br, 19·9. $C_{17}H_{20}BrAs$ requires Br, 21·1%).

When the arsinoline was treated with 1 mol. of bromine, and the product with alkali, no *As*-oxide could be detected. The main product was γ-phenylpropyl bromide.

As-*Chlorotetrahydroarsinoline.*—*As*-Methyltetrahydroarsinoline (20 g.) was dissolved in carbon tetrachloride, and a current of dry chlorine allowed to impinge on the surface of the solution. The white solid *dichloride* separated rapidly, and when a slight excess of chlorine was present the mixture was rendered colourless by addition of a drop of arsinoline. The carbon tetrachloride was removed by distillation, and the residue distilled under diminished pressure. Evolution of methyl chloride was regular and rapid, and as soon as it was complete a preliminary fraction distilled at 120—150°/21 mm., and then the whole of the residue at 155°/16 mm. (16 g.). The latter crystallised on cooling, to give large, irregular, hexagonal

rhombs, m. p. 22°, and was pure As-*chlorotetrahydroarsinoline* (Found : Cl, 15·4. $C_9H_{10}ClAs$ requires Cl, 15·5%).

When a solution of the chloroarsine in diethylaniline was boiled for 5 hours, marked decomposition occurred, but no 3 : 4-dihydroarsinoline was isolated from the product. A small quantity of an arsine was formed, since the distilled product combined or reacted with methyl iodide.

Benzyldimethylarsine.—Magnesium benzyl chloride reacted smoothly with one equivalent of dimethyliodoarsine. The product was worked up in the usual manner. The final ethereal solution remained clear while being dried over sodium sulphate, but, when filtered, became cloudy. This was due to oxidation and not to the presence of an additive compound with dimethyliodoarsine, since the ethereal solution had, in accordance with usual practice, been washed with alkali. The arsine was finally obtained as a colourless liquid, b. p. 110°/8 mm. The yield (20%) would probably be improved by carrying out all the operations in an inert atmosphere (compare Turner and Bury, *loc. cit.*).

The *methiodide* is formed readily, and separates from alcohol in colourless leaflets, m. p. 195—196° (Found : I, 37·4. $C_{10}H_{16}IAs$ requires I, 37·6%). The *ethiodide*, formed moderately readily, crystallises from alcohol–ether in colourless leaflets, m. p. 163—165° (Found : I, 36·3. $C_{11}H_{18}IAs$ requires I, 36·1%).

δ-*Phenyl*-n-*butyldimethylarsine.*—This was prepared from γ-phenylpropyl bromide, *via* the corresponding nitrile (von Braun, *Ber.*, 1910, **43**, 2843; Rupe, *Annalen*, 1912, **395**, 87), δ-phenyl-*n*-butyl alcohol, and δ-phenyl-*n*-butyl bromide (von Braun, *Ber.*, 1911, **44**, 2871).

The bromide readily formed a Grignard reagent; this reacted smoothly with dimethyliodoarsine to give a product which, after the usual treatment, including washing with alkali, afforded the arsine as a colourless liquid, b. p. 150°/14 mm. (yield, 45%).

The *methiodide* is very readily formed, and is sparingly soluble in alcohol, from which it crystallises in colourless leaflets, m. p. 150—151° (Found : I, 33·0. $C_{13}H_{22}IAs$ requires I, 33·4%).

The *ethiodide*, formed moderately easily, separates from alcohol in leaflets, m. p. 134—135° (Found : I, 32·5. $C_{13}H_{24}IAs$ requires I, 32·2%).

Phenyl-β-*phenylethylmethylarsine.*—This substance was readily obtained by the interaction of magnesium β-phenylethyl bromide and phenylmethyliodoarsine in ethereal solution. When the ethereal extract of the arsine, obtained by the usual method, was evaporated, a considerable quantity of a gummy solid separated. This was removed before distilling the arsine under diminished

pressure. *Phenyl-β-phenylethylmethylarsine* is a colourless liquid boiling at 187°/12 mm. and 190°/15 mm., and was obtained in 82% yield.

The *methiodide* is formed readily, and crystallises from water in rhombohedra or prisms, m. p. 119° (Found: I, 30·5. $C_{16}H_{20}IAs$ requires I, 30·6%).

Action of β-Phenylethyl Bromide on Arsenites and Arsinites.—(a) *On sodium arsenite.* A solution of arsenious oxide (0·5 mol.) in aqueous sodium hydroxide (3 mols.) was boiled with the bromide for several days, under reflux. Some bromide was recovered unchanged, and no arsinic acid could be detected in the product. (b) *On sodium arsenite in presence of copper bronze.* The bromide was stirred and heated at 140—180° for 7 hours in presence of dry sodium arsenite (Kahlbaum) and copper bronze. No change was observed. (c) *On potassium methylarsinite.* An aqueous-alcoholic solution containing methylarsenious oxide (1 mol.), potassium hydroxide (2 mols.), and the bromide (1 mol.) was boiled under reflux for 2 days. Styrene, but no arsinic acid, was formed.

[With F. W. BURY.] *Dicyclohexylphenylarsine.*—This was prepared by adding phenyldichloroarsine to a solution of magnesium *cyclo*hexyl bromide, the reaction product being worked up in the usual manner. The arsine is a colourless liquid, b. p. 220°/14 mm. The *methiodide* and *ethiodide* are formed readily and crystallise from alcohol–ether in prisms, m. p. 187° (Found: I, 27·5. $C_{19}H_{30}IAs$ requires I, 27·6%), and plates, m. p. 188—189° (Found: I, 26·6. $C_{20}H_{32}IAs$ requires I, 26·8%), respectively.

Tricyclohexylarsine.—When arsenious iodide was added to an ethereal solution of magnesium *cyclo*hexyl chloride or bromide, only half of the calculated quantity reacted. The arsine was, however, obtained mixed with a little di*cyclo*hexyl as a colourless oil, b. p. 235°/12 mm. The *methiodide* was formed readily and crystallised from water in prisms, m. p. 153—154°. The *benzobromide* melts at 197° with slight decomposition (Found: Br, 16·2. $C_{25}H_{40}BrAs$ requires Br, 16·2%).

cyclo*Hexylphenylmethylarsine.*—A Grignard reagent prepared from 24 g. of *cyclo*hexyl chloride was treated with phenylmethyliodoarsine until the yellow colour of the latter persisted, *i. e.*, when about 75% of the iodo-compound had been added. The reaction product was worked up as usual, and gave 30 g. of cyclo*hexylphenylmethylarsine* as a highly refractive oil, b. p. 152—153°/12 mm., having no marked tendency to oxidise.

When the arsine was heated at 100° with one equivalent of benzyl bromide and a little alcohol, large, colourless crystals began to form, but subsequently disappeared. On cooling, only a little white

powder separated, and crystallisation was induced by addition of excess of ether. cyclo*Hexylphenylbenzylmethylarsonium bromide* was thus obtained; recrystallised from alcohol–ether, it formed rectangular plates, m. p. 193° (Found: Br, 19·0. $C_{20}H_{26}BrAs$ requires Br, 19·0%).

The corresponding d-*α-bromocamphor-π-sulphonate* was prepared. The crude material melted at 109—113°, and crystallisation experiments gave unpromising results, mixtures of crystalline, amorphous, and gel-like material being obtained.

Phenylbenzylarsinic Acid.—Excellent yields of this acid are obtained by the following method, which is more expeditious than that described by Bertheim (*Ber.*, 1915, **48**, 350): Crude phenylarsenious oxide (75 g.) as obtained from phenyldichloroarsine and sodium hydroxide was dissolved in 150 c.c. of methylated spirit. Sodium hydroxide (36 g.) in 52 c.c. of water was added. To the hot solution, 60 g. of benzyl chloride were added gradually, keeping the initial vigorous reaction in progress. Sodium chloride separated at once. The mixture was left until cold, freed from alcohol by distillation, acidified, and the resulting precipitate of acid washed with water and ether.

Strychnine Phenylbenzylarsinate.—This salt was prepared by mixing hot alcoholic solutions of the base and the acid, and formed colourless needles (Found: N, 4·5; As, 11·4, 11·4.

$$C_{21}H_{22}O_2N_2,C_{13}H_{13}O_2As,3H_2O$$

requires N, 4·2; As, 11·3%). It had $[\alpha]_D^{20°}$—31·2° in 50% aqueous acetone, and when crystallised from this solvent gave a mixture of free acid and strychnine salt. When hot alcoholic solutions of strychnine (1 mol.) and the acid (2 mols.) were mixed, the free acid separated first.

l-*Menthylamine Phenylbenzylarsinate.*—Equivalent quantities of the base and acid were together dissolved in alcohol, and the solution was allowed to evaporate in a vacuum over sulphuric acid. The whole set to a mass of hairy needles. These were collected, dissolved in benzene, and the solution treated with light petroleum; a crystalline precipitate was obtained, which consisted of a mixture of base and acid.

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CLXXXIX.—*The Resin of* Hevea *Rubber.*

By George Stafford Whitby, Jacob Dolid, and Frederic Harrison Yorston.

The circumstance that the resin of the rubber from *Hevea brasiliensis* constitutes only a small proportion of the weight of the rubber (on the average, about 2·80%. Compare van Rossem, *Koll.-Chem. Beih.*, 1918, **10**, 52; "The Quality of Plantation Rubber," Imp. Inst., 1922, pp. **13**, **27**, **88**, **95**) and is of a sticky, semi-fluid consistency has apparently deterred investigators from subjecting it to chemical examination (compare, *e.g.*, Tschirch and Müller, *Arch. Pharm.*, 1905, **243**, 141), and when the present investigation was begun but little was known concerning its chemical nature.

It has now been shown that, contrary to Hinrichsen and Kindscher's statement (*Z. angew. Chem.*, 1910, **23**, 49), the resin contains several optically active substances (all lævorotatory, with the exception of an amino-acid occurring in very small amounts only) and that sterol substances are present. Hillen's failure to obtain sterol colour reactions (*Arch. Pharm.*, 1913, **251**, 94) was probably due to interference of other substances present in the crude extract. Cohen (*Arch. Pharm.*, 1908, **246**, 520) examined the resin for lupeol, with negative results. Hinrichsen and Kindscher (*loc. cit.*) found the resin to be largely saponifiable, and Dekker (*Koll.-Chem. Beih.*, 1918, **10**, 54), who confirmed this finding, obtained the data shown in the first two columns below. The figures in the third column, which have been added, would seem to suggest that the differences in the percentage of extract unsaponifiable in different forms of *Hevea* rubber are due to differences in the amount of saponifiable matter rather than to differences in the amount of unsaponifiable matter.

Form of rubber.	Acetone extract %.	% extract unsaponifiable.	% unsaponifiable in the rubber.
Fine hard Para	3·0	25·4	0·76
Sheet	1·8	48·3	0·87
Crêpe	3·2	22·0	0·705

A sample of the resin was found by Hinrichsen and Kindscher (*loc. cit.*) to show an iodine absorption of 118%. Beadle and Stevens (*Internat. Cong. Appd. Chem.*, 1912, **24**, 581) reported that the resin was partly water-soluble. The presence in it of nitrogenous material was mentioned by Spence and Kratz (*Kolloid-Z.*, 1914, **14**, p. 268, footnote), and was confirmed by Dekker (*Meded. Delft*, 1916, 506) by an indirect method. Dekker found acetone extraction to reduce the nitrogen content of two samples of *Hevea* crêpe by 0·051 and 0·029%, respectively, and of a sample of *Hevea* sheet by 0·014%.

Working with a sufficiently large amount of the acetone extract of *Hevea* rubber, the present authors have isolated and identified a sterol, a sterol ester, a sterol glucoside, *d*-valine, quebrachitol, and stearic acid and the liquids, oleic and linoleic acids. The amounts and ratios in which the substances occur vary in different rubber samples. The mixture of unsaturated, liquid fatty acids occurs in much larger amount than any of the other constituents. Titration of the acetone extract of twenty-four samples of smoked sheet and pale crêpe rubber showed that the average total acid content was equivalent to 0·272 g. of potassium hydroxide per 100 g. of rubber. Hence, if the mean molecular weight of the acids is taken as 280, the total acid content of average samples of latex *Hevea* rubber is of the order of 1·4% of the weight of the rubber or roughly one-half of the weight of the acetone extract.

The total amount of solid material which it was actually possible to crystallise from the extract was about 0·65% of the weight of the rubber. As the resin content of the crêpe from which most of the resin examined was obtained was 2·71%, it may be said that of this about 1·9 (=1·25 + 0·65) was definitely accounted for. The balance of about 0·8% represented losses together with unidentified constituents of the liquid, uncrystallisable portion of the resin.

The order of magnitude (%) in which the recognised constituents of *Hevea* resin occurred was estimated roughly as follows :

Sterol ester	0·075	Quebrachitol	very small amount
Sterol glucoside	0·175	Stearic acid	0·15
Sterol	0·225	Oleic acid, Linoleic acid	1·25
d-Valine	0·015		

The high proportion of free fatty acid in the resin of *Hevea* rubber makes this resin unique, not only among the resins of rubbers of various botanical origins, but also among resins in general. In *Hevea* resin, fatty acids predominate, and hence it has a softer consistency, a higher saponification value, and a smaller optical activity than have other rubber resins, in which optically active, unsaponifiable, crystalline substances predominate. The resins obtained by extracting plants with organic solvents contain free fatty acids in a good many cases, but never in large proportions (Power and his co-workers, J., various papers).

The question of the mode of association of the resin constituents with the hydrocarbon in rubber is of some interest. It is probable that the fatty acids occur in solution in the caoutchouc. Rubber, both raw and vulcanised, swells considerably when placed in oleic acid, linoleic acid, molten stearic acid, or the mixed liquid fatty acids actually isolated from *Hevea* rubber. Thus, for example, a sample of smoked sheet placed in the last-mentioned medium

imbibed 4·04 times its weight after 7 days. The sterol glucoside found in rubber is insoluble in all the usual laboratory solvents, including benzene. It probably occurs, not dissolved in the caoutchouc, but in solution in the fatty acids, for the authors have observed that it will dissolve on warming in fatty acids, except in the lowest members, yielding sols which often gel on cooling.

The resin, and especially the fatty acids which it comprises, influence the behaviour of rubber in several important ways (compare Whitby, *Trans. Inst. Rubber Ind.*, 1925, **1**, 12; Whitby and Jane, *Second Colloid Symposium Monograph*, 1925, 16).

Experimental.

Samples of rubber were extracted with acetone in a large, heavily galvanised iron extractor of the Soxhlet type, 3 ft. high and 1 ft. in diameter. The thimble, which is large enough to hold about 4·5 kg. of rubber, is suspended directly in the vapour of the boiling extractant. The condenser, which sits on a flange at the top of the main extraction vessel, consists of a hollow cone and head through which water circulates and a separate, conical coil of block tin round the cone. The metal of the extractor was attacked slightly in the course of time, zinc salts of fatty acids being found in the extract.

The extracts from a number of different samples of rubber (crêpe, smoked sheet, slab crêpe) were examined. The procedure varied somewhat in different cases, as the proportions of the constituents were not identical in different batches, but in general it was as follows: The batch of rubber was extracted for 70 to 100 hours. The solution was concentrated to about 600 c.c. per kg. of rubber and kept for a week or so at or below 0°. The solid which separated (Fraction A) was removed and the solution (and washings) was concentrated to one-third or less of its volume and again kept in the cold for a week. The solid which separated (Fraction B) was removed and washed with a little cold acetone. The solution and washings were then evaporated on the water-bath to remove as much acetone as possible. The viscous liquid residue is called the Liquid Fraction.

Fraction A.

This fraction (47 g. of a light brown powder from 21·7 kg. of pale latex crêpe) was separated into a chloroform-soluble sterol ester, a water-soluble amino-acid and quebrachitol, and an insoluble sterolin.

Sterol Ester.—Chloroform extracted from fraction A about 10 g. of a sterol ester which, after recrystallisation from alcohol, had m. p. 83° and $[\alpha]_D^{24°}$ — 11·1°, — 10·8° (0·2145 and 0·2303 g. in 15 c.c.

of chloroform) (Found: C, 83·0; H, 12·6; iodine absorption, 34·3. $C_{17}H_{33}O_2 \cdot C_{27}H_{45}$ requires C, 82·8; H, 12·4; iodine absorption, 39·6%). The iodine absorption is due to unsaturation of the sterol part of the ester, the acid part being saturated. (The iodine values obtained for sterols are usually somewhat lower than the calculated values.) The *sterol* obtained by hydrolysing the ester with alcoholic potassium hydroxide crystallised from alcohol in fine, white needles, m. p. 133—134°, $[\alpha]_D^{21°}$ − 23·2° (0·3140 g. in 15 c.c. of chloroform) (Found: C, 82·8; H, 11·4. $C_{27}H_{46}O$ requires C, 83·9; H, 11·9%) and gave the usual colour reactions and also certain new reactions (Whitby, *Biochem. J.*, 1923, **17**, 5). The acetate crystallised from alcohol in matted crystals, m. p. 113—114°, and gave $[\alpha]_D^{18°}$ − 18·8° (0·1707 g. in 15 c.c. of chloroform). The *acid* obtained by hydrolysis of the sterol ester melted at 73—75° after recrystallisation from alcohol and appeared to have the composition $C_{17}H_{34}O_2$ (Found: C, 74·5; H, 11·2. Calc.: C, 75·6; H, 12·6%. Found for the *silver* salt: Ag, 28·5. $C_{17}H_{33}O_2Ag$ requires Ag, 28·5%).

The sterol ester isolated from slab rubber and from smoked sheet melted at 102° and 91—93°, respectively, but the amounts isolated were insufficient for careful examination.

The Aqueous Extract.—Addition of alcohol to the concentrated aqueous extract of fraction A (derived from 21·7 kg. of crêpe) precipitated 1 g. of an amino-acid; quebrachitol remained in solution. The two substances could also be separated by precipitating the amino-acid with mercuric nitrate or by evaporating the aqueous extract to dryness and extracting the amino-acid with cold alcoholic hydrochloric acid.

The amino-acid, m. p. about 260° (decomp.), gave (*a*) the ninhydrin reaction, (*b*) the pine splinter pyrrole reaction, when heated either alone or with zinc dust, and (*c*) a blue colour with phenol and sodium hypochlorite (Found: C, 52·2; H, 9·42; amino-N, by micro-van Slyke method, 11·7, 11·6. $C_5H_{11}O_2N$ requires C, 51·3; H, 9·4; N, 11·9%). It had $[\alpha]_D^{25°}$ +22·9°; $[\alpha]_D^{16°}$ +26·5° (0·1888 g. in 25 c.c. of 20% HCl). For a 3% solution of *d*-valine in 20% HCl, E. Fischer (*Ber.*, 1906, **39**, 2325) obtained $[\alpha]_D^{16°}$ +28·8°. The total amino-nitrogen in an aqueous extract of the original rubber was 0·0015% (micro-van Slyke method). This corresponds to 0·0126% of valine in the rubber or 0·46% of valine in the acetone extract.

Quebrachitol was first noticed as separating in well-formed crystals from the acetone extract of a sample of smoked sheet which had stood for a long time after the separation of a first fraction. It had m. p. 190° and $[\alpha]_D^{20°}$ −80·3° (0·2800 g. in 14·5 c.c. of water).

It was subsequently always recognised in fraction A, and in several cases was actually isolated from it.

By means of Scherer's test for inositol (*Annalen*, 1852, **81**, 375; compare Boedker, *Ztg. nat. Med.*, **10**, 162) the presence of quebrachitol was detected in forty-five samples of *Hevea* rubber comprising all the usual forms (latex crêpe, lower grade crêpes, smoked sheet, fine hard Para, etc.). For most of these samples the authors are indebted to Dr. O. de Vries. A few grams of the rubber (as little as 1 g. will give a positive result), cut into small pieces, were boiled for 15—30 minutes with glacial acetic acid, which was then evaporated, finally on a water-bath. The material extracted from the residue by a little hot water developed a rose-red colour after the usual nitric acid–calcium chloride treatment.

The isolation of quebrachitol from the latex of *H. brasiliensis* has been recorded by De Jong (*Rec. trav. chim.*, 1906, **25**, 48), and from rubber by Pickles and Whitfield (P., 1911, **27**, 54).

Professor R. P. D. Graham has kindly made crystallographic measurements on some of the crystals which separated from the acetone extract and on larger crystals of quebrachitol which had grown in a sample of evaporated latex serum which had been kept for 9 years. For comparison, there are given below the crystallographic data obtained by Anderson with a sample of quebrachitol isolated by Petrie from *Heterodendron oleæfolium*, Desf. (*Proc. Linnean Soc. N.S. Wales*, 1918, **43**, 857).

Crystallographic data for l-*inositol methyl ether* (by R. P. D. Graham). The crystals were transparent, colourless blades, sometimes attaining a length of 6 mm. or more. *System* : orthorhombic. No cleavage was observed. *Forms and habit* : All the crystals measured exhibited the forms *a*(100), *b*(010), *m*(110), and *q*(011). On several of the crystals there were in addition very small facets of the form (101). The crystals were elongated in the direction of the vertical axis, and tabular parallel to *a* or *m*. The faces of the orthorhombic prism, *m*, were heavily striated vertically, with a tendency to curvature; but faces of the other forms were smooth and yielded fair reflexions. A peculiarity of the crystals was that, in nearly all the cases observed, only two opposite faces of the prism *m* were developed.

Angular measurements and axial ratios.

	Limits.	No.	Mean.	Calc.	Anderson.
b m	52° 26′—53° 19′	5	52° 47′		52° 44′
c q	39 10—39 35	6	39 22		39 26
c	47° 03′	1	47 03	47° 13′	47 43

Axial ratios $a : b : c = 0{\cdot}7595 : 1 : 0{\cdot}8204$
$0{\cdot}7609 : 1 : 0{\cdot}8224$ (Anderson).

The Sterolin.—The residue of fraction A after removal of the chloroform- and water-soluble portions consisted in all cases of sterol glucoside. After purification through its acetate, it had m. p. 285—290° (decomp.) and $[\alpha]_D^{20°}$ — 41·7° (0·2900 g. in 14·6 c.c. of pyridine) (Found : C, 73·0; H, 10·4. $C_{33}H_{56}O_6$ requires C, 72·3; H, 10·2%). Its behaviour in the sterol colour reactions and in a new test which enables sterolins to be distinguished from sterols has been described elsewhere (Whitby, *Biochem. J.*, 1923, **17**, 5). The *acetate*, prepared by means of hot acetic anhydride, crystallised from alcohol in pearly leaflets, m. p. 165°; $[\alpha]_D^{20°}$ — 22·4 (Found : C, 69·1; H, 9·0; Ac, 23·1. $C_{33}H_{52}O_6Ac_4$ requires C, 68·7; H, 8·9; Ac, 22·5%). The *benzoate* was prepared by treating a pyridine solution of the sterolin with a slight excess of benzoyl chloride, extracting the diluted reaction mixture with ether, and washing the extract with dilute sulphuric acid, dilute potassium hydroxide, and water in succession. The product, recrystallised from ether, had m. p. 198° and $[\alpha]_D^{20°}$ + 15·7°, + 16·1° (0·3256, 0·2637 g., respectively, in 15 c.c. of chloroform).

Hydrolysis of the sterolin by hydrochloric acid in amyl alcohol by Power and Salway's method (J., 1913, **103**, 399) gave glucose (osazone, m. p. 201°) and a sterol. The latter, obtained as lustrous plates after recrystallisation, melted at 134·5° and had $[\alpha]_D^{20°}$ — 31·7°, — 32·1° (0·2793 and 0·1268 g., respectively, in 15 c.c. of chloroform) (Found : C, 84·3; H, 12·3. $C_{27}H_{46}O$ requires C, 83·9; H, 11·9%). The acetate of this sterol melted at 115° and showed $[\alpha]_D^{20°}$ —38·6° (0·0634 g. in 15 c.c. of chloroform). There is little doubt that the sterolin is sitosterol *d*-glucoside (Power and Salway, *loc. cit.*, p. 1022).

The sterol glucosides are soluble, not only in hot amyl alcohol and in pyridine (Power and Salway, *loc. cit.*, p. 399), but also in amines (piperidine and diethylamine), fatty acids (octoic acid), mustard oils (phenylthiocarbimide), and higher ethers (anisole). In many of such liquids the sols set to gels on cooling.

Fraction B.

This fraction usually consisted of a mixture of a sterol or sterols and one or more saturated fatty acids. Separation was effected by treating the mixture with alcoholic potassium hydroxide and then extracting the sterol by ether from the mixture of potassium salt and sterol which came out on cooling. In certain cases, either the sterol or the fatty acid predominated so greatly that recrystallisation was sufficient to obtain it in a pure condition.

The Sterol.—A sterol was first isolated from the acetone extract of a batch of 4 kg. of smoked sheet rubber, which, when concentrated to 500 c.c. per kg. and kept in the cold, deposited 9 g. of

almost pure sterol as rosettes of crystals. After recrystallisation six times from alcohol, there was obtained a mass of matted, white leaflets, m. p. 125°, $[\alpha]_D^{23.5°}$ —24·6° (0·2975 g. in 15 c.c. of chloroform) (Found : C, 83·8; H, 13·0. $C_{27}H_{46}O$ requires C, 83·9; H, 11·9%).

Fischer's method (*Ber.*, 1913, **46**, 4029) of preparing penta-acyl derivatives of sugars is suitable for the acylation of sterols, including cholesterol. The *benzoate :* The sterol described above was treated in chloroform solution with a slight excess of benzoyl chloride and an equivalent amount of quinoline. After a short time, the solution was washed successively with dilute sulphuric acid, dilute sodium hydroxide solution, and water, dried over calcium chloride, and the chloroform evaporated. The residue crystallised from alcohol–chloroform in lustrous plates, m. p. 144—145°; $[\alpha]_D^{22°}$ — 20·7° (0·1340 g. in 14·6 c.c. of chloroform) (Found: C, 83·9; H, 9·9. $C_{27}H_{45}\cdot O\cdot CO\cdot C_6H_5$ requires C, 83·3; H, 10·2%). *The propionate*, prepared by a similar method, crystallised from alcohol in lustrous white plates, m. p. 98°; $[\alpha]_D^{23°}$ — 29·4° (0·2005 g. in 17 c.c. of chloroform). The *acetate*, prepared by treating the sterol with an excess of acetic anhydride, was obtained as white plates or leaflets, m. p. 114—115°; $[\alpha]_D^{22°}$ — 30·6° (0·3169 g. in 14·6 c.c. of chloroform).

A sample of sterol obtained, in the case of a batch of 21·7 kg. of pale latex crêpe, by extracting a mixture of potassium soap and sterol with ether was freed from potassium salt by converting this into the silver salt and extracting the sterol with ether. After several recrystallisations from ether, the sterol was obtained as lustrous plates, m. p. 134—135°; $[\alpha]_D^{20°}$ — 21·4° (0·3278 g. in 15 c.c. of chloroform). The *benzoate* had m. p. 144·5°, and $[\alpha]_D^{24°}$ — 12·5° (0·2393 g. in 15 c.c. of chloroform) (Found : C, 83·1; H, 10·2. $C_{34}H_{50}O_2$ requires C, 83·3; H, 10·2%).

From the acetone extract of a sample of slab rubber, not quite the whole of the sterol separated when the extract was kept at a suitable concentration. The extract was then saponified, and from the unsaponifiable material ether removed a sterol, m. p. 133—134°.

The Fatty Acid.—The main fatty acid present in fraction B, previously regarded as a C_{20} saturated fatty acid and named " heveïc acid " (Whitby, *Brit. Assoc. Rep.*, 1923, 432), has now been identified as stearic acid. A sample (equiv., 291) isolated from slab rubber melted at 65·5—66·5° after recrystallisation from alcohol and at 68·5° after recrystallisation from aqueous acetic acid, benzene, aqueous acetone, and light petroleum in succession. It was then mixed with further quantities of solid acid obtained from crêpe rubber, recrystallised until its melting point was 67·5—68·5°, and converted, by treatment of the silver salt with ethyl

iodide in benzene, into the ethyl ester. This after purification had m. p. 32·5—33·5° and $n_D^{40°}$ 1·4292. The acid regenerated therefrom had m. p. 68—69° (alone or mixed with stearic acid), $n_D^{70°}$ 1·4332, $n_D^{80°}$ 1·4300 ($n_D^{70°}$ for stearic acid in the same apparatus, 1·4328). A sample of the ester prepared from the solid acid derived from another sample of rubber had, after distillation and recrystallisation from chloroform, m. p. 31·5° (Found : *M*, 314. Calc. : *M*, 312).

Another sample of the chief solid acid was isolated from the acetone extract of a sample of latex crêpe rubber as follows : The mixture of the crystallisable substances which separated on allowing the extract, slightly diluted with acetone, to stand for several months was extracted with chloroform. The residue left on removal of the chloroform was separated by several crystallisations from alcohol and ethyl acetate into (*a*) a sterol ester (less soluble) and (*b*) a fatty acid (more soluble). The latter after several recrystallisations melted at 67—69° and had an equivalent weight of 295. It was purified further through its barium salt and then, after recrystallisation from acetone, aqueous acetic acid, and chloroform, had m. p. 68·5—69·5° (Found : equiv. by titration, 293, 289).

The Liquid Fraction.

This fraction was distilled with steam, which removed the last traces of acetone and also mesityl oxide, evidently formed from the acetone during the extraction. No essential oil was present. After removal of the non-volatile oil with ether, the aqueous layer contained a small amount of nitrogenous material precipitable by alkaloidal reagents; phosphomolybdic acid precipitated 2·5 g. (from 21·7 kg. of crêpe rubber) and in the case of slab crêpe, the precipitate given by platinic chloride contained 24·0% of platinum and did not melt at 295°. Both precipitates gave the pyrrole test on ignition.

The Liquid Fraction consisted preponderantly of unsaturated fatty acids, although some evidence was obtained of the presence of a magnesium salt. After steam distillation the fraction was esterified by hydrogen chloride in methyl alcohol at 0°, the ester mixture distilled, and the fraction, b. p. 195°/9 mm.—185°/5 mm., saponified. The free acid thus obtained had, after removal of a little crystalline material, a mean molecular weight (by titration) of 317 and an iodine absorption (Hübl) of 140, 141. *Hydrogenation.* 8·63 G. were treated with purified hydrogen in ether in presence of platinum-black carried on finely-divided barium sulphate. Unfortunately, some of the alkaline sodium hyposulphite solution over which the hydrogen was stored was sucked into the reaction flask, and in consequence only 619 c.c. of hydrogen were taken up

instead of the 1100 c.c. corresponding to the iodine value. Nevertheless, pure stearic acid was isolated in such good yield and so easily that it may be considered certain that only C_{18} unsaturated acids were present in the liquid submitted to hydrogenation. The crystals obtained after evaporation of the ether had m. p. 68·5° after recrystallisation from ethyl acetate and 69—69·5° after further recrystallisation from alcohol and from chloroform (Found : equiv., 281, 284). A total of 3·66 g. of stearic acid was isolated and the final mother-liquor left on evaporation 2·34 g. of impure stearic acid. *Oxidation.* The potassium soaps from 3 g. of the mixed acids were oxidised in aqueous solution with 3 g. of potassium permanganate. That part of the product which was soluble in cold ether was extracted with carbon tetrachloride. The portion thus extracted melted at 60° after recrystallisation, and was probably impure saturated acid. The portion (0·05 g.) unextracted by the carbon tetrachloride melted at 124—126°, had a molecular weight by titration of about 320, and was probably dihydroxystearic acid (*vide infra*). (A sample of dihydroxystearic acid prepared from Kahlbaum's oleic acid melted at 128° after several recrystallisations.) That part of the product which was insoluble in cold ether amounted, after recrystallisation from aqueous alcohol, to 0·42 g. and melted at 160—170°. By extracting it with boiling water, crystals were obtained, m. p. 155—156°, having an equivalent weight (by titration) of 356 and probably representing sativic acid. *Bromination.* A sample of the mixed acids was brominated in cold ethereal solution by Muggenthaler's method. No ether-insoluble bromide was obtained, and hence linolenic acid was absent. A small amount of a bromide melting, after recrystallisation from light petroleum, at 112° was obtained. (Linoleic acid tetrabromide melts at 113—114°.)

In order to identify the liquid acids with greater certainty, the solvent was removed from the acetone extract of 11 kg. of latex crêpe rubber, and the residue was boiled with water, in order to eliminate any mesityl oxide and to extract water-soluble constituents. The material was then boiled with 5% potassium hydroxide solution in excess of the amount equivalent to the acid known to be present in the rubber, and, after most of the material had gone into solution, the liquid was evaporated and distributed on pumice. This was then dried on a steam-bath and extracted with light petroleum, which removed, in addition to sterol and other unsaponifiable material, some potassium linoleate. This salt separated on cooling and after recrystallisation was obtained as a pale yellow powder (21 g.), which rapidly became brown in the air. Oxidation with potassium permanganate converted it

into sativic acid, insoluble in light petroleum or ether, melting at 165° after one recrystallisation from alcohol, and having an equivalent weight of 338 (sativic acid, 348). The pumice was now boiled with water and the acids liberated from the soap solution thus obtained were washed and dried [Found : *M* (mean), 340, 340. Iodine absorption, 144, 145%]. The potassium salts derived from 19 g. of the acids gave, on oxidation with permanganate : (*a*) 0·95 g., soluble in light petroleum, melting at 45—60° after two recrystallisations, and probably representing impure saturated acid; (*b*) 0·85 g. of dihydroxystearic acid (white crystals, m. p. 128—130°. Found : C, 67·8; H, 11·8%); (*c*) 2·7 g. of sativic acid. The last was separated by fractional crystallisation into portions, m. p. 169·5° and 154°, respectively. Nicolet and Cox (*J. Amer. Chem. Soc.*, 1922, **44**, 144) have shown that the two *dl*-mixtures of tetrahydroxystearic acids formed by the oxidation of linoleic acid can be separated by fractional crystallisation, the melting point of one being 171° and of the other 153°.

The zinc salt of a fatty acid was left on the pumice after the extraction of the soaps. It melted at 123°, and was probably impure zinc stearate derived from the zinc of the galvanised iron extractor and the stearic acid of the resin. A specimen of the zinc salt prepared from a somewhat impure sample of the solid acid isolated from the resin (m. p. 67—69°), by heating the acid in cymene solution with zinc oxide, melted at 123°.

Hence the presence of oleic and linoleic acids in the Liquid Fraction can be regarded as established; and, since further only C_{18} acids are present, it seems safe to assume that the higher liquid fatty acids in rubber consist of oleic and linoleic acids exclusively. The purest sample of the mixed liquid fatty acids isolated showed an iodine absorption of 140 (*vide supra*). As this sample probably contained a small amount of solid acid as impurity, it is probable that the amount of linoleic acid present is considerably more than twice that of oleic acid. This conclusion is supported by the relative yields of dihydroxy- and tetrahydroxy-stearic acids obtained on oxidation.

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CXC.—*Some Fatty Acid Derivatives.*

By GEORGE STAFFORD WHITBY.

This paper describes the use of the silver salts of the fatty acids (which are obtainable by a convenient procedure described in the experimental part) for the preparation of derivatives such as the glycerides, acid anhydrides, and esters by double decomposition with appropriate halogen compounds. Certain mixed triglycerides have been prepared by treating β-acyl dichlorohydrins with such silver salts:

$$RCO{\cdot}O{\cdot}CH(CH_2Cl)_2 \xrightarrow{2R'CO_2Ag} RCO{\cdot}O{\cdot}CH(CH_2{\cdot}O{\cdot}COR')_2.$$

β-Acyl dichlorohydrins can be prepared by the action of acyl chlorides not only on α-dichlorohydrin, but also on epichlorohydrin: *i.e.*, acyl chlorides add on to epichlorohydrin in the same sense that hydrogen chloride does, the chlorine assuming the α-position:

$$CH_2Cl{\cdot}CH\!\!<\!\!\begin{matrix}CH_2\\O\end{matrix}\!\!> + R{\cdot}COCl = CH_2Cl{\cdot}CH(O{\cdot}COR){\cdot}CH_2Cl.$$

This has been shown to be the case for propionyl, butyryl, and stearyl chlorides.

The silver salts of the fatty acids react very easily with acyl chlorides, yielding acid anhydrides, and readily with alkyl halides, yielding esters. In a homologous series of esters of palmitic acid and in a similar series of esters of stearic acid, the melting point falls from the methyl ester to a minimum in the butyl ester.

Heintz (*Ann. Phys.*, 1852, **87**, 21, 267; 1854, **92**) concluded that the fatty acids derived from the saponification of spermaceti comprised stearic acid. The present author has isolated cetyl stearate from spermaceti by fractional crystallisation.

EXPERIMENTAL.

Silver Salts of Fatty Acids.—Silver salts of both higher and lower fatty acids were obtained as fine, white powders, which suffered no discoloration when kept for 3 years in the light, by the following procedure: To a 2—4% alcoholic solution of the acid were added, in either order, 1 equiv. of aqueous ammonia (*d ca.* 0·9) and 1 equiv. of silver nitrate (dissolved in twice its weight of water; or dissolved in its own weight of water, and the warm solution diluted with alcohol). After 2—3 hours, the precipitate was filtered off, dried on a porous plate, powdered, and, if desired, dried at 50° for several hours. In the case of the higher fatty acids, the silver salt was precipitated in a more easily filterable form at about 50° than at room temperature. The yields were almost theoretical. Silver

stearate, palmitate, laurate, myristate, hexoate, butyrate, propionate, acetate, and oleate prepared by this procedure were shown to be pure by determining their silver content. The stearic acid used melted at 69·5°, and the palmitic acid at 62·5°.

From the higher fatty acids, silver salts were also obtained as white powders, stable in the light, by a modification of Krafft's method (*Ber.*, 1888, **21**, 2266); the precipitates, however, were contaminated with a small amount (usually about 1%) of the free fatty acid, which could be removed by washing with alcohol or extraction with ether: Silver nitrate (1 equiv.) dissolved in a little water was treated with sufficient aqueous ammonia to re-dissolve the precipitate formed. The solution was added to an alcoholic solution of the fatty acid, precipitation completed by the addition of water, and the readily-filterable silver salt washed with alcohol and dried on a porous plate.

The solubility of silver palmitate and stearate in water at 20°, determined colorimetrically (Whitby, *Z. anorg. Chem.*, 1910, **67**, 68), was 0·00123 g. and 0·00065 g., respectively, per litre. These two salts therefore fall in line with the silver salts of the lower acids, the solubilities of which change from member to member in a comparatively regular manner (Lieben, *Monatsh.*, 1884, **15**, 404). Silver palmitate and stearate being less soluble than silver chloride, sodium chloride does not precipitate silver chloride from a solution of silver palmitate or stearate, held up by the minimum quantity of ammonia. Silver palmitate, being more soluble than silver stearate, requires less ammonia to cause it to dissolve in alcohol, and, conversely, it requires more water to precipitate it from ammoniacal alcoholic solution.

The silver salts of the higher fatty acids swell, disperse, and, on cooling, yield gels in various organic liquids, *e.g.*, aromatic hydrocarbons, on heating (compare Whitby, *Science*, 1921, **53**, 580). Silver oleate yields gels more readily than does silver palmitate or stearate. Thus it gives a gel in benzene, whereas silver stearate requires the higher-boiling xylene to yield a firm gel; in toluene, it gives only a weak gel, and in benzene it merely swells. Silver oleate gives a weak gel in amyl alcohol. In *n*-propyl alcohol, it swells and disperses, but on cooling separates as flocks, not as a gel. Gelation in organic liquids can be obtained at a lower point in the fatty acid series in the case of the silver than in the case of the alkali salts. Thus, silver hexoate dissolves in hot xylene and on cooling the sol will set to a weak gel, whereas potassium and sodium hexoates remain undispersed in boiling xylene.

β-Acyl Dichlorohydrins.

The α-dichlorohydrin used was prepared by the action of fuming hydrochloric acid on epichlorohydrin.

β-Butyryl Dichlorohydrin.—(a) A mixture of 29·58 g. of α-dichlorohydrin and 23·72 g. of butyryl chloride was, after the initial reaction had subsided, warmed at 50° to complete the reaction, moisture being excluded (loss, 7·95 g. Calc., 7·82 g.). Distillation yielded a product, b. p. 223·5°, having a fruity odour, $n_D^{20°}$ 1·4540, $d_{20°}^{20°}$ 1·1796, saponification number 843 (Calc. for $C_7H_{12}O_2Cl_2$, 845·5). (*b*) A mixture of 23·05 g. of epichlorohydrin and 29·05 g. of butyryl chloride (*ca.* 10% excess) was heated under reflux for 8 hours at 75°, the entry of moisture being prevented. The twice-distilled product had b. p. 223·5°, $n_D^{20°}$ 1·4540, $d_{20°}^{20°}$ 1·1792, saponification number 841·5. Truchot (*Compt. rend.*, 1865, **61**, 1170) gives b. p. 226°/738 mm. and $d_4^{11°}$ 1·194.

β-Propionyl dichlorohydrin was prepared in similar ways to those mentioned above, except that in (*b*) the mixture of epichlorohydrin and propionyl chloride was heated in a sealed tube at 135° for 3 hours. The methods gave identical products, b. p. 208°, $d_{20°}^{20°}$ 1·2222.

β-Palmityl Dichlorohydrin.—Reaction between 13·79 g. (*ca.* 20% excess) of α-dichlorohydrin and 22·15 g. of palmityl chloride was completed by heating the mixture for 1 hour in a boiling water-bath (loss, 2·93 g. Calc., 2·94). The product, which set solid on cooling, crystallised from alcohol in white crystals, m. p. 34·4°, $n_D^{50°}$ 1·4527 [Found: saponification number, 456·7; Cl, 19·2 (by saponification), 19·1 (by Carius). $C_{19}H_{36}O_2Cl_2$ requires Cl, 19·3%; saponification number, 458·7]. Palmitic acid isolated after saponification, 68·97 (calc., 69·76%).

β-Stearyl Dichlorohydrin.—(a) This was prepared from α-dichlorohydrin and stearyl chloride in the manner described for the preparation of β-palmityl dichlorohydrin. It had m. p. 39·5° and $n_D^{50°}$ 1·4528 (Found: saponification number, 424·1; Cl, 17·8. $C_{21}H_{40}O_2Cl_2$ requires Cl, 17·85%; saponification number, 426·0). Stearic acid isolated after saponification, 72·18 (calc., 71·91%). (b) 20·8 G. of stearyl chloride were heated with 6·8 g. of epichlorohydrin in a sealed tube at 130° for 3½ hours. The product, on recrystallisation from alcohol, readily yielded pure β-stearyl dichlorohydrin. It contained a small amount of material of low melting point and very slight solubility in alcohol, the nature of which was not investigated. $n_D^{50°}$, 1·4530. Saponification number, 423.

Mixed Triglycerides.

β-*Palmitodistearin* (β-*Palmityl αα′-distearyl glyceride.*)—(a) Powdered β-palmityl dichlorohydrin (1 mol.) and silver stearate (2 mols.) were mixed and heated either for 3 hours at 155° or for 5 hours at 135°. An ethereal extract of the product slowly deposited the fat as a pale cream, microcrystalline solid, m. p. 63·5°, and 64·8° after recrystallisation from ether; the crystals from the mother-liquor had the same melting point. $n_D^{70°}$ 1·4467. Mean dispersion (n_F—n_C), 0·00788. Saponification number, 196·2 ($C_{55}H_{106}O_6$ requires 195·2). 1·6269 G. of the mixed silver salts prepared, by the method described earlier, from the mixed fatty acids obtained on saponification gave 0·4595 g. of silver (calc., 0·4593 g.). Freedom of the product from stearic or palmitic acid was shown by the fact that addition of silver nitrate followed by ammonia to an alcoholic solution produced no precipitate. The fat was practically insoluble in cold alcohol.

(*b*) The glyceride was also prepared from β-palmityl dichlorohydrin and silver stearate, reacting in hot phenetole for 2½ hours. The filtrate, on cooling, deposited the fat as rosettes or sheaves of needles, m. p. 64°. After recrystallisation from ether, the product agreed in melting point and saponification number with that described above.

The m. p. of β-palmitodistearin is given as 63° by Kreis and Hafner (*Ber.*, 1903, **36**, 2766) and Bömer and Limprick (*Z. Nahr. Genussm.*, 1913, **25**, 354) and as 67·1° by Amberger and Bromig (*Biochem. Z.*, 1922, **130**, 252).

β-*Stearodipalmitin* (β-*stearyl αα′-dipalmityl glyceride*) was prepared from β-stearyl dichlorohydrin and silver palmitate by method (a). M. p. 63·3° (Amberger and Bromig, *loc. cit.*, give 59·1°). Saponification number, 202·6 ($C_{53}H_{102}O_6$ requires 201·8).

β-*Butyrodipalmitin* (β-*Butyryl αα′-dipalmityl glyceride*).—With the aid of some ether, silver palmitate (2 mols.) and β-butyryl dichlorohydrin (1 mol.) were mixed. The ether was removed by warming on the water-bath, and the mixture heated at 170° for ½ hour with occasional stirring. When cold, the product was extracted with ether, silver chloride filtered off, and the ether removed. The residue was dissolved in alcohol and treated with the quantity of alcoholic potassium hydroxide necessary to neutralise the free acid present. The alcohol was then removed at 40° under reduced pressure, the residue extracted with dry chloroform, the chloroform removed, and the product recrystallised from alcohol. It then had m. p. 43·6°, $n_D^{60°}$ 1·4431, $n_D^{70°}$ 1·4397, $n_D^{80°}$ 1·4359; saponification number, 265·6 ($C_{41}H_{74}O_6$ requires 263·3). 100 G. of absolute alcohol at 20° dissolve 0·55 g. of β-butyrodipalmitin.

β-*Palmitodibutyrin* (β-*Palmityl αα'-dibutyryl glyceride*).—An intimate mixture of β-palmityl dichlorohydrin (1 mol.) and silver butyrate (2 mols.) was heated at 150° for 40 minutes, being stirred at intervals. The procedure used to isolate β-butyrodipalmitin was then followed. It was necessary to cool the alcoholic solution in ice in order to obtain crystals. These had m. p. 17°, and 18° after recrystallisation from alcohol. $n_D^{20°}$ 1·4530. Saponification number, 388 ($C_{27}H_{50}O_6$ requires 385·1).

Acid Anhydrides.

Propionic Anhydride—Silver propionate (31·8 g.) and propionyl chloride (16·25 g.) developed considerable heat on mixing. No propionyl chloride came over on distillation. The yield of the crude anhydride was 20·0 g. (88%), and on redistillation this gave 80% of pure propionic anhydride, b. p. 165°.

Butyric Anhydride.—(a) From silver butyrate and butyryl chloride in the manner just described, a good yield of butyric anhydride, b. p. 193°, was obtained. (b) Lachowiz's method of preparing acetic and propionic anhydrides (*Ber.*, 1884, **17**, 1218; 1885, **18**, 2920) gave a poorer yield of butyric anhydride than method (a). A mixture of 40 c.c. of butyryl chloride and 600 g. of powdered lead nitrate (dried at 100°) was heated on the water-bath under reflux for 2—3 hours; it was then extracted with dry benzene, and the extract distilled. By several redistillations of the fraction b. p. 165—200°, a 50% yield of butyric anhydride was obtained.

Palmitic Anhydride.—A mixture of 6·40 g. of palmityl chloride and 8·19 g. of silver palmitate was heated and stirred on the water-bath for 10 minutes, and, when cold, was extracted with anhydrous ether. The product, recrystallised from ether, had m. p. 62·6°. Another sample had m. p. 63·0° after recrystallisation from benzene. Saponification number, 226; *M*, cryoscopic in benzene, 402 [$(C_{15}H_{31}\cdot CO)_2O$ requires saponification number 226·8; *M*, 394]. 100 G. of absolute alcohol at 20° dissolve 0·18 g. of palmitic anhydride.

Stearic Anhydride.—This was prepared from stearyl chloride and silver stearate in a similar way to that just described. After recrystallisation from ether, the substance was obtained as large, shining plates, similar in appearance to stearic acid. M. p. 70·5°. Saponification number, 202·5; *M*, cryoscopic in benzene, 540 [$(C_{17}H_{35}\cdot CO)_2O$ requires saponification number, 203·7; *M*, 550·7]. 100 G. of absolute alcohol at 20° dissolve 0·023 g. of stearic anhydride. The solubility in ether was clearly less than that of stearic acid.

The anhydrides of palmitic and stearic acids, although very similar to the corresponding acids in melting point and appearance, are much less soluble and have higher refractive indices. The following measurements were all made with the same instrument.

Refractive indices of some fatty acids and their anhydrides.

Propionic acid : $n_D^{17°}$ 1·3874.	Propionic anhydride : $n_D^{17°}$ 1·4041.
n-Butyric acid : $n_D^{18°}$ 1·3990.	*n*-Butyric anhydride : $n_D^{18°}$ 1·4143.
Palmitic acid : $n_D^{70°}$ 1·4309.	Palmitic anhydride : $n_D^{70°}$ 1·4359.
Stearic acid : $n_D^{80°}$ 1·4300.	Stearic anhydride : $n_D^{80°}$ 1·4362.

Esters of Palmitic and Stearic Acids.

Cetyl Palmitate : Cetyl Stearate.—These were prepared by heating a mixture of the appropriate silver salt (made from a sample of the pure acid) and recrystallised cetyl iodide (m. p. 21·9°) in a boiling water-bath for ½ hour, with stirring at intervals. The reaction mixture was extracted with ether, silver iodide filtered off, and the ethereal solution allowed to deposit crystals. The yields were practically theoretical, and the products, which consisted of lustrous, white plates, were so pure that recrystallisation from ether or glacial acetic acid failed to change the original melting point. Saponification numbers : cetyl palmitate, 117·0 ($C_{15}H_{31}\cdot CO_2\cdot C_{16}H_{33}$ requires 116·7); cetyl stearate, 111·1 ($C_{17}H_{35}\cdot CO_2\cdot C_{16}H_{33}$ requires 110·3). Both esters were readily soluble in acetone, carbon disulphide, or chloroform, and were very soluble in benzene. Ethereal solutions were occasionally supersaturated, but crystallisation was immediately induced by touching with ice a point in the vessel.

	Cetyl palmitate.	Cetyl stearate.
Melting point	51·6°	56·6°
$n_D^{60°}$, $n_D^{65°}$	1·4429, 1·4415	—
$n_D^{70°}$	1·4398	1·4410
100 G. of abs. ether dissolve at 22°	21·01 g.	9·08 g.
,, ,, ,, ,, 0°	2·30 g.	0·73 g.
,, ,, alcohol ,, 22°	0·0495 g.	0·0594 g.
,, glacial acetic acid dissolve at 22°	0·0633 g.	0·0388 g.
Turbidity temperature (Valenta test, with 2 c.c. of glacial acetic acid and 2 c.c. of ester)	109°	Turbid to b. p.

Cetyl Stearate from Spermaceti.—400 G. of a sample of spermaceti (m. p. 42—44°; $n_D^{70°}$ 1·4397; turbidity temperature 77°; saponification number 125·8; iodine absorption 5·89%) were recrystallised from ether nineteen times; 2·2 g. were obtained of a product with a constant melting point of 56·6° and agreeing in saponification number, refractive index, and turbidity temperature with cetyl stearate. On the basis of determinations of the amount and melting point of the material in the mother-liquors from the successive

crystallisations, and of determinations of the melting point of artificial mixtures of cetyl palmitate and cetyl stearate, a rough estimate of the amount of cetyl stearate in the sample of spermaceti examined was made as 1·1%. A second sample of spermaceti was also examined. 1200 G. (original m. p. 41—44°) yielded, after ten crystallisations, 1·5 g. of crystals, m. p. 55·5°, having a saponification number of 111·5 (calc., 110·5) and giving cetyl alcohol (m. p. 50° after several recrystallisations from alcohol) and stearic acid (m. p. 65° after three recrystallisations from alcohol) on hydrolysis.

Benzyl Palmitate.—Equivalent quantities of silver palmitate and benzyl chloride were heated, with stirring at intervals, for ½ hour at 145°. The ester was extracted with ether and recrystallised from alcohol. M. p. 36° (compare Shonle and Row, *J. Amer. Chem. Soc.*, 1921, **43**, 361). $n_D^{70°}$ 1·4620. 100 G. of absolute alcohol at 16° dissolve 3·30 g.

Benzyl stearate was prepared similarly to benzyl palmitate. M. p. 44·3° (Shonle and Row, *loc. cit.*, give m. p. 45·8°), $n_D^{70°}$ 1·4627. 100 G. of absolute alcohol at 16° dissolve 0·685 g.

Homologous Series of Esters.—The esters the physical constants of which are recorded in the following table were prepared from the appropriate silver salt and alkyl halide. In the case of methyl stearate, ethyl palmitate, and ethyl stearate a mixture of equivalent amounts of the silver salt and the alkyl iodide was gradually heated in xylene to 100° and maintained at that temperature for about 10 minutes. Silver iodide was filtered off, and washed with hot xylene. The xylene solution was, if necessary, concentrated under reduced pressure, the ester allowed to crystallise, and then recrystallised from alcohol to a constant melting point.

				Saponification number.	
Palmitate.	M. p.	$n_D^{30°}$.	$n_D^{78°}$.	Found.	Calc.
Ethyl	23·5°	1·4278	1·4200	204	197·3
n-Propyl	20·4	1·4290	1·4211	186	188·1
n-Butyl	16·9	1·4312	1·4232	179·5	179·7
n-Amyl	19·4	1·4320	1·4241	171	172
*iso*Amyl	12·5	1·4315	1·4236	175	172
n-Octyl	22·5	1·4358	1·4277	152	152·3
Stearate.					
Methyl	38·8°				
Ethyl	33·6	1·4320	1·4238	182	179·5
n-Propyl	30·5	1·4323	1·4242	174	171·9
n-Butyl	27·5	1·4328	1·4250	165·9	164·8
n-Amyl	30	1·4342	1·4266	160	158·3
*iso*Amyl	23	1·4333	1·4260	160	158·3
n-Octyl	31·8	1·4373	1·4300	143	141·5

In the case of the other esters listed, with the exception of the octyl esters, reaction was brought about by heating a mixture

of equivalent quantities of the silver salt and the alkyl iodide alone, without xylene, for 1½ hours at 100°. The product was extracted with hot alcohol. In the case of the octyl esters a mixture of the silver salt and octyl bromide was heated for 2½ hours at 130—140°.

Both in the palmitate and in the stearate series the melting point reaches a minimum in the *n*-butyl esters, but the refractive index increases continuously.

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CXCI.—*The Conditions underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part VIII. Products derived from Pimelic Acid. An Application of Bischoff's Dynamic Hypothesis.*

By Albert Hassell and Christopher Kelk Ingold.

In general, the action of alkalis on the α-halogen derivatives of dibasic acids proceeds in three ways. Thus, monobromoglutaric acid yields a hydroxy-acid (I), a ring-acid (II), and an unsaturated acid (III), in addition to substances derived from the decomposition of these.

$CH_2<\begin{matrix}CH(OH)\cdot CO_2H\\CH_2\cdot CO_2H\end{matrix}$ (I.) $\quad CH_2<\begin{matrix}CH\cdot CO_2H\\|\\CH\cdot CO_2H\end{matrix}$ (II.) $\quad CH<\begin{matrix}CH_2\cdot CO_2H\\CH\cdot CO_2H\end{matrix}$ (III.)

If the quantity of unsaturated acid formed is small, the reaction may be regarded as a competition between hydroxylation and ring-formation, and may be used to estimate the relative ease of ring-formation in the different cases. This method has been applied to a number of glutaric and adipic acids, with results explicable on the assumption that the volumes of groups attached to a central carbon atom determine the inclination of its valencies and the consequent tendency of that atom to participate in a ring of given type (Ingold, J., 1921, **119**, 305, and later).

The halogen derivatives of pimelic acid have now been investigated, and, despite the fact that in this case there are difficulties in the way of a precise numerical comparison, the general results accord with the hypothesis. The ring formed is a five-membered one, and the ratio (ring-formation) : (hydroxylation) is much greater than in any case previously investigated.

In the case of the αα′-dihalogen-adipic esters (IV), concentrated

alkalis gave a small quantity of a *cyclo*butene acid (VI), and a considerable amount of muconic acid (VII) and of the hydroxy-acids (V).

$$CO_2R\cdot CHBr\cdot CH_2\cdot CH_2\cdot CHBr\cdot CO_2R \quad \text{(IV.)}$$

$CH_2\cdot CH(OH)\cdot CO_2H$ / $CH_2\cdot CH(OH)\cdot CO_2H$ (V; two forms.) $\qquad$ $CH_2\cdot C(=CH_2)\cdot CO_2H$ / $CH_2\cdot C\cdot CO_2H$ (VI.) $\qquad$ $CH{:}CH\cdot CO_2H$ / $CH{:}CH\cdot CO_2H$ (VII.)

When $\alpha\alpha'$-dibromopimelic ester (VIII) was examined, a greatly increased tendency to ring formation was noticed Under various conditions, a considerable proportion of the material was transformed into the *cyclo*pentene acid (IX), although this acid did not always survive the conditions of its formation. When concentrated alkalis were employed, a second principal reaction gave rise to a doubly-unsaturated open-chain acid (X) (see below); the question as to whether this undergoes subsequent isomeric change is discussed below. So far as could be ascertained, dihydroxypimelic acids were not produced.

$CH_2<$ $CH_2\cdot CHBr\cdot CO_2R$ / $CH_2\cdot CHBr\cdot CO_2R$ (VIII.) $\qquad$ $CH_2<$ $CH_2\cdot C(=CH_2)\cdot CO_2H$ / $CH_2\cdot C\cdot CO_2H$ (IX.) $\qquad$ $CH_2<$ $CH{:}CH\cdot CO_2H$ / $CH{:}CH\cdot CO_2H$ (X.)

The constitution of the ring-acid (IX) follows from its identity with the acid synthesised by Haworth and Perkin (J., 1894, **65**, 978) from the saturated *cyclo*pentane acid (XI), the dibromo-ester (XII) of which, on treatment with potassium iodide, yielded the ester (XIII):

$$CH_2<\begin{matrix}CH_2\cdot CH\cdot CO_2H\\ CH_2\cdot CH\cdot CO_2H\end{matrix}\ \text{(XI.)} \longrightarrow CH_2<\begin{matrix}CH_2\cdot CBr\cdot CO_2R\\ CH_2\cdot CBr\cdot CO_2R\end{matrix}\ \text{(XII.)} \longrightarrow CH_2<\begin{matrix}CH_2\cdot C(=CH_2)\cdot CO_2R\\ CH_2\cdot C\cdot CO_2R\end{matrix}\ \text{(XIII.)}$$

In the presence of concentrated alkalis, the unsaturated ring-acid (IX) undergoes change into the isomeric acid (XIV), the reaction being analogous to the conversion of citraconic acid into itaconic acid, and of Δ^1-tetrahydrophthalic acid into the Δ^2-acid. The change is not complete, and definite evidence of its reversibility has been obtained. At the same time, a small amount of the saturated hydroxy-ring acid (XV) is produced.

(XIV.) $CH_2<$ $CH=C(CO_2H)$ / $CH_2\cdot CH\cdot CO_2H$ $\qquad$ $CH_2<$ $CH_2\cdot C(OH)\cdot CO_2H$ / $CH_2\cdot CH\cdot CO_2H$ (XV.)

It is noteworthy that whereas the *cyclo*propane hydroxy-ring acid (XVI) is quantitatively converted into the isomeric ketoglutaric acid (XVII) by alkalis (Ingold, *loc. cit.*), the hydroxy*cyclo*pentane acid (XV) shows no tendency to pass into α-ketopimelic acid

(XVIII). The two cases evidently represent the two limiting conditions of the keto-cyclol change.

$$CH_2\!<\!\begin{matrix}C(OH)\cdot CO_2H\\ CH\cdot CO_2H\end{matrix} \longrightarrow CH_2\!<\!\begin{matrix}CO\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix} \qquad CH_2\!<\!\begin{matrix}CH_2\cdot CO\cdot CO_2H\\ CH_2\cdot CH_2\cdot CO_2H\end{matrix}$$

(XVI.) (XVII.) (XVIII.)

Although formula (X) must represent the structure of the unsaturated open-chain acid initially produced from dibromopimelic ester, it is possible that this acid changes into the isomeride (XIX) under the conditions of the experiment. It is known that under these conditions αβ-unsaturated acids readily come into equilibrium with their βγ-unsaturated isomerides, and in this case the βγ-compound possesses a conjugated system from which it might be expected to derive sufficient stability to render the isomeric change practically non-reversible. The acid appears to be identical with the "piperylenedicarboxylic acid" obtained by Willstätter (*Ber.*, 1895, **28**, 3287) by the exhaustive methylation of tropinic acid (XX):

$$\text{(XX.)}\quad \begin{matrix}CH_2\cdot CH\cdot CH_2\cdot CO_2H\\ |\quad\quad >NMe\\ CH_2\cdot CH\cdot CO_2H\end{matrix} \longrightarrow \begin{matrix}CH{:}CH\cdot CH_2\cdot CO_2H\\ |\\ CH{:}CH\cdot CO_2H\end{matrix} \qquad \text{(XIX.)}$$

These reactions do not, of course, prove the structure, but the tendency to the production of conjugated systems by the exhaustive methylation process is well known, and is illustrated by the exhaustive methylation of piperidine.

A remarkable reaction, which has not been observed in any of the shorter-chain series previously investigated, is that which leads to the formation of considerable quantities of the meso- and racemic forms of the dimethoxy-acid $CO_2H\cdot CH(OMe)\cdot[CH_2]_3\cdot CH(OMe)\cdot CO_2H$ when methyl-alcoholic potassium hydroxide is employed as the hydrolysing agent. Although the occurrence of this reaction creates difficulties when the attempt is made to extend to the pimelic acid series the method of numerical comparison previously employed, it is in accord with the view that the conditions governing all these reactions are essentially spatial; for whereas steric influences would prevent the accumulation of as many as four bulky groups (2MeO and $2CO_2H$) in 1 : 5- and 1 : 6-positions, there is no obstacle in the way of their occupying 1 : 7-positions, and hence this reaction is not encountered in the glutaric and adipic acid series, and is met with for the first time in the pimelic acid series. It may be predicted that the occurrence of this reaction, under the conditions specified, will be found to be a peculiarity of the higher series, and that it will be prominent in the suberic and azelaic acid series.

EXPERIMENTAL.

Pimelic acid was prepared by hydrolysis of the ethyl pentanetetracarboxylate produced from ethyl sodiomalonate and $\alpha\gamma$-dibromopropane. It was dibrominated in the form of its chloride, and the dibromo-chloride converted into ethyl dibromopimelate, which was treated with 6*N*-methyl-alcoholic potassium hydroxide, as in the previous investigations of this series. The acid product, a pale yellow syrup, was dissolved in water, neutralised with ammonia, and a concentrated aqueous solution of lead acetate was added in four or five successive portions until no further precipitation occurred, the solutions being kept cold throughout. The various fractions of lead salt were collected separately and decomposed with a small excess of dilute sulphuric acid, the filtrates from the lead sulphate being concentrated in a vacuum and extracted with ether. The acid regenerated in this way from the first fraction of lead salt solidified almost completely, and some of the intermediate fractions, on being seeded with the solid and kept for some weeks, deposited crystals. These fractions were then again submitted to the fractional precipitation of lead salts, and some further crops of crystalline acid were thus obtained.

Piperylenedicarboxylic Acid (XIX).—The solid acid, after two crystallisations from ether, melted at 169° (Found: C, 53·7; H, 5·3. $C_7H_8O_4$ requires C, 53·8; H, 5·1%), and corresponded closely in its properties with the acid obtained by Willstätter by exhaustive methylation of tropinic acid. The yield of purified material was 6·2% of the theoretical. The tetrabromide melted with decomposition at 217° (Found: Br, 67·0. Calc.: Br, 67·2%).

On oxidation with eight atoms of available oxygen in the form of 4% permanganate at the ordinary temperature, a small amount of malonic acid and much oxalic acid were obtained. On reduction by a large excess of sodium amalgam in boiling aqueous solution, a semi-solid product was obtained from which pimelic acid was isolated by draining and crystallisation from ether.

cyclo*Pentanol*-1 : 2-*dicarboxylic Acid* (XV).—The syrupy acids recovered from the lead salts, together with those obtained from the aqueous filtrates by extraction with ether after acidification, and desiccation over potassium hydroxide to remove acetic acid, were dissolved in ether and extracted with successive small quantities of water. The first extract, on evaporation in a vacuum, gave a residue which in course of time partly solidified. The remaining extracts gave syrups. The solid was drained (5·5% unpurified) and crystallised from acetone–benzene, from which it separated in small prisms, m. p. 159—160° (Found: C, 48·6; H, 5·8. $C_7H_{10}O_5$ requires C, 48·2; H, 5·7%).

The *silver* salt was prepared from the neutral ammonium salt (Found: Ag, 55·5. $C_7H_8O_5Ag_2$ requires Ag, 55·7%).

The *ethyl* ester was prepared by boiling the silver salt with ethyl iodide in ether solution; b. p. 168—171°/10—11 mm. (Found: C, 57·1; H, 7·8. $C_{11}H_{18}O_5$ requires C, 57·4; H, 7·8%). On heating with acetic anhydride in a sealed tube at 180°, an oil was obtained which, on hydrolysis by hydrochloric acid, gave *cyclo*pentene-1 : 2-dicarboxylic acid, m. p. 178°.

Δ^1-cyclo*Pentene*-1 : 2-*dicarboxylic Acid* (IX).—The syrupy residues from the ethereal and the various aqueous solutions obtained in the preceding separation were combined and esterified with ethyl alcohol and sulphuric acid. The esters, after several distillations, yielded a fraction, b. p. 146°/11 mm., which was hydrolysed by boiling with hydrochloric acid under a condenser sufficiently short to permit the escape of alcohol vapour. On evaporation of the aqueous solution, a solid product was obtained, which melted indefinitely at 140—150°, and after several crystallisations from water yielded a small quantity of the Δ^1-*cyclo*pentene acid, which was identified by analysis (Found: C, 53·9; H, 5·1. Calc.: C, 53·8; H, 5·1%) and by a mixed melting point determination.

Δ^2-cyclo*Pentene*-1 : 2-*dicarboxylic Acid* (XIV).—This acid appears to be the main constituent of the mixture, m. p. 140—150° (19% of the theoretical yield), but the separation of the last traces of the 178°-acid necessitates several alternate crystallisations from water and ethyl acetate. This acid is very much more soluble in water than the Δ^1-isomeride; it separates from water or ethyl acetate in small prisms, m. p. 146—147° (Found: C, 53·5; H, 5·1. $C_7H_8O_4$ requires C, 53·8; H, 5·1%).

2 : 3-*Dibromo*cyclo*pentane*-1 : 2-*dicarboxylic acid* was obtained when the Δ^2-acid was exposed to bromine vapour for several days. The product, after being freed from bromine, was crystallised twice from glacial formic acid, from which it separated in small, dense prisms, which decompose with much frothing at 165° (Found: Br, 50·4. $C_7H_8O_4Br_2$ requires Br, 50·6%).

On heating for a few minutes with boiling 64% aqueous potassium hydroxide, both the Δ^1- and Δ^2-*cyclo*pentene acids yield a mixture consisting mainly of the Δ^2-acid, along with a small amount of the Δ^1-acid. In one experiment, starting with the Δ^1-acid, a small amount of the hydroxy-ring acid was also isolated. The method of separation of these mixtures was substantially the same as that already described.

Ethyl $\alpha\alpha'$-*Dimethoxypimelate*.—In the distillation of esters (above) a large fraction (35% of the theoretical yield) was obtained, b. p. 160—175°/10 mm. This consisted essentially of a mixture of the

meso- and racemic forms of the dimethoxy-ester, and the central fraction, b. p. 166—169°/10 mm., gave correct figures on analysis (Found: C, 56·8; H, 8·7. $C_{13}H_{24}O_6$ requires C, 56·5; H, 8·7%).

Both the central fraction and the main fraction (the former, b. p. 166—169°/10 mm., and the latter, b. p. 160—175°/10 mm.), on hydrolysis by means of hydrochloric acid, gave a syrupy acid which could not be induced to crystallise, although it yielded a silver salt having the correct silver content for the dimethoxy-compound (Found: Ag, 50·2. $C_9H_{14}O_6Ag_2$ requires Ag, 49·8%). It was therefore digested with a small excess of pure thionyl chloride until sulphur dioxide ceased to be evolved, and after the excess of reagent had been removed at 100°, the acid chloride was treated with dry ammonia in ether solution. This process yielded a mixture of two crystalline amides.

The esters, b. p. 160—175°/10 mm., were mixed with concentrated aqueous ammonia (3 vols.), and the mixture was shaken frequently until it became homogeneous (3—6 days).

αα′-Dimethoxypimelamide (A-form).—This amide crystallised practically completely from the aqueous ammonia solution. It melted at 209—210°, and after one crystallisation from water was obtained pure, as prisms, m. p. 212°. The mixture of amides obtained from the ethereal ammonia solution yielded the A-amide in a pure condition after two crystallisations from water (Found: C, 49·2; H, 8·3. $C_9H_{18}O_4N_2$ requires C, 49·5; H, 8·3%). The amide is readily soluble in hot water, sparingly soluble in cold, fairly easily soluble in methyl or ethyl alcohol or acetone, and almost insoluble in ethyl acetate, chloroform, or benzene.

αα′-Dimethoxypimelamide (B-form).—The ammonia solution from the esters, after the A-amide had been collected, was evaporated on the water-bath until, on cooling, it set to a stiff paste of crystals, which were drained on porous porcelain and crystallised from water and ethyl acetate; the compound separated in fluffy balls of minute needles, m. p. 167°. The aqueous solution from the decomposition of the acid chlorides, after the A-amide had been removed, was evaporated to dryness, and the residue extracted from the ammonium chloride with boiling ethyl acetate, from which, on concentration and cooling, the B-amide separated almost pure. It was crystallised from ethyl acetate (Found: C, 49·3; H, 8·2%). This amide is extremely soluble in hot water and very easily soluble in cold; it is fairly easily soluble in hot ethyl acetate, but almost insoluble in cold; it is easily soluble in acetone or methyl or ethyl alcohol, but insoluble in chloroform or benzene.

αα′-Dimethoxypimelic Acid (A-form).—A solution of the A-amide (1 g.) in 10 c.c. of concentrated sulphuric acid was treated between

0° and 5° with a strong aqueous solution of 0·6 g. of sodium nitrite delivered by a fine capillary tube dipping beneath the liquid, the addition occupying about 1·5 hours, during which the mixture was continually stirred. The solution was poured into water and extracted with ether, from which the A-acid was obtained as a clear gum (Found: C, 49·0; H, 7·3. $C_9H_{16}O_6$ requires C, 49·1; H, 7·3%. Found for the *silver* salt: Ag, 49·6. $C_9H_{14}O_6Ag_2$ requires Ag, 49·8%).

αα′-Dimethoxypimelic Acid (B-form).—This acid was prepared similarly from the B-amide and had similar properties (Found: C, 49·1; H, 7·4%. Found for the *silver* salt: Ag, 49·5%).

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CXCII.—*The Conditions underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part IX. Products derived from Suberic and Azelaic Acids.*

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ACCORDING to the hypothesis underlying this series of investigations, the action of concentrated methyl-alcoholic alkali on ethyl αα′-dibromosuberate should pursue a course similar to that observed in the pimelic acid series.

The bromination of suberic acid has been investigated by Gauthier, Hell, and Rempel (*Ber.*, 1882, **15**, 149; 1885, **18**, 814), who isolated a dibromo-acid of m. p. 173°. αα′-Dibromosuberic acid (I) should exist in meso- and racemic modifications, and a second form, m. p. 118–120°, has now been isolated. Both forms are produced together in the ordinary Hell-Volhard process of bromination, the less fusible acid in the greater quantity.

It appears impossible at present to assign configurations to these two acids, because, on treatment with dilute alkalis, both yield the same αα′-dihydroxysuberic acid (II), so that in one case or the other an inversion must occur at one of the two asymmetric carbon atoms.

$$[CH_2]_4\begin{<}{CHBr\cdot CO_2H \atop CHBr\cdot CO_2H}\ (\textit{two forms}) \longrightarrow [CH_2]_4\begin{<}{CH(OH)\cdot CO_2H \atop CH(OH)\cdot CO_2H}\ (\textit{one form})$$

(I.) (II.)

By the action of alcoholic alkali on the less fusible dibromo-acid, Hell and Rempel (*loc. cit.*) obtained an acid, $C_8H_{10}O_4$, which

they termed "suberocolic acid," but they were unable to ascertain whether it was a doubly unsaturated open-chain acid (III) or a *cyclo*hexene acid such as (IV). It has now been found that the acid has an open-chain structure, for, on partial reduction, it forms a dihydro-derivative which is still unsaturated, and on vigorous reduction gives suberic acid.

$$\begin{array}{l}CH_2\cdot CH{:}CH\cdot CO_2H\\ CH_2\cdot CH{:}CH\cdot CO_2H\end{array}\quad (III.) \qquad \begin{array}{l}CH_2\cdot CH_2\cdot C\cdot CO_2H\\ CH_2\cdot CH_2\cdot C\cdot CO_2H\end{array}\quad (IV.) \qquad \begin{array}{l}CH_2\cdot CH{=}C\cdot CO_2H\\ CH_2\cdot CH_2\cdot CH\cdot CO_2H\end{array}\quad (V.)$$

The acids (IV) and (V) are, however, produced along with (III) when ethyl dibromosuberate is treated with concentrated alkalis under the conditions described in the experimental part of this paper. It is probable that (IV) is the first product, although it changes into (V) to a large extent under the conditions employed in its formation.

The cyclic acids had previously been prepared by the reduction of benzene derivatives, and Baeyer observed the conversion of (IV) into (V) by the action of alkalis (*Annalen*, 1890, **258**, 209). He appears, however, to have regarded the change as complete, whereas, actually, the action is a balanced one, the acid (V) undergoing limited conversion into (IV) under identical experimental conditions.

When methyl-alcoholic alkali is used, considerable quantities of the meso- and racemic forms of the dimethoxy-acid

$$CO_2H\cdot CH(OMe)\cdot[CH_2]_4\cdot CH(OMe)\cdot CO_2H \quad (VI.)$$

are produced in agreement with the prediction made in the preceding paper.

The general rules deduced in the preceding parts of this series suggest that the principal product of the action of concentrated methyl-alcoholic alkali on ethyl $\alpha\alpha'$-dibromoazelate (VII) should be the dimethoxy-acid (VIII) (in which the methoxyl groups occupy 1 : 9-positions) and that the by-products, if any, should consist of the dihydroxy-acid (IX) and the unsaturated acid (X). Further, it is not to be expected that *cyclo*heptane ring closure would take place to any considerable extent, although some might occur, as in the *cyclo*butane series (Part II); an acid of constitution (XI) (if formed) might pass into its open-chain ketonic isomeride (XII).

$$CH_2\!<\!\begin{array}{l}CH_2\cdot CH_2\cdot CHBr\cdot CO_2Et\\ CH_2\cdot CH_2\cdot CHBr\cdot CO_2Et\end{array}\quad (VII.) \qquad CH_2\!<\!\begin{array}{l}CH_2\cdot CH_2\cdot CH(OMe)\cdot CO_2H\\ CH_2\cdot CH_2\cdot CH(OMe)\cdot CO_2H\end{array}\quad (VIII.)$$

$$(IX.)\ CH_2\!<\!\begin{array}{l}CH_2\cdot CH_2\cdot CH(OH)\cdot CO_2H\\ CH_2\cdot CH_2\cdot CH(OH)\cdot CO_2H\end{array} \qquad CH_2\!<\!\begin{array}{l}CH_2\cdot CH{:}CH\cdot CO_2H\\ CH_2\cdot CH{:}CH\cdot CO_2H\end{array}\ (X.)$$

$$CH_2\!<\!\begin{array}{l}CH_2\cdot CH_2\cdot C(OH)\cdot CO_2H\\ CH_2\cdot CH_2\cdot CH\cdot CO_2H\end{array}\quad (XI.) \qquad CH_2\!<\!\begin{array}{l}CH_2\cdot CH_2\cdot CO\cdot CO_2H\\ CH_2\cdot CH_2\cdot CH_2\cdot CO_2H\end{array}\quad (XII.)$$

The experiments now described show that under the conditions of hydrolysis which have been uniformly employed during these investigations the dibromo-ester (VII) is converted to the extent of at least 80% into a mixture of meso- and racemic methoxy-acids of formula (VIII) in striking agreement with the conclusions summarised in the preceding paper. Considerable difficulty was experienced in isolating the by-products of the reaction, but the dihydroxy-acid (IX) was obtained as a mixture of meso- and racemic isomerides, and an unsaturated acid, which may have been (X), was present. The production of the ring-acid (XI) could not be established with certainty, but an acid which appears to have the open-chain ketonic structure (XII) was isolated.

Experimental.

Suberic acid was prepared from castor oil, as described by Baker and Ingold (J., 1923, **123**, 128).

αα′-Dibromosuberic Acid (*A-form*).—Suberic acid (60 g.) was warmed with 60 c.c. of thionyl chloride until sulphur dioxide ceased to be evolved, and the product treated on the steam-bath with 45 c.c. of bromine, added gradually to keep pace with the absorption. The product was poured into absolute formic acid and boiled until carbon monoxide ceased to be evolved; on cooling, 60 g. of the dibromo-acid, m. p. 160—170°, separated. After two crystallisations from water, this acid melted at 172—173° (Found: Br, 48·3. Calc.: Br, 48·2%).

αα′-Dibromosuberic Acid (*B-form*).—The formic acid mother-liquors were evaporated, and the pasty residue was drained on porous porcelain, and extracted with boiling chloroform until the m. p. of the undissolved portion rose above 160°. (This, after crystallisation from water, yielded a further 6 g. of the A-acid.) The residue from the chloroform solution was drained and crystallised several times from the same solvent; 20 g. of B-acid, m. p. 120—121°, were thus obtained (Found: Br, 48·0. $C_8H_{12}O_4Br_2$ requires Br, 48·2%).

Ethyl αα′-Dibromosuberate.—Suberic acid (60 g.) was brominated as before, and the product poured into ethyl alcohol. The ester was extracted with ether after the addition of water, washed with dilute sodium carbonate solution, and distilled. It boiled constantly at 230°/31 mm., the yield being almost theoretical (Found: Br, 41·0. $C_{12}H_{20}O_4Br_2$ requires Br, 41·2%).

αα′-Dihydroxysuberic Acid.—This substance is formed when either the A- or the B-form of αα′-dibromosuberic acid is boiled with 2*N*-aqueous sodium carbonate. The product, which is extracted with ether after acidification, is purified through the barium salt,

and thus obtained as a colourless gum which sets to a hard, crystalline mass, m. p. 166—168°, during the course of several months (Found: C, 46·8; H, 6·8. $C_8H_{14}O_6$ requires C, 46·6; H, 6·8%).

Suberocolic Acid.—Ethyl αα′-dibromosuberate was treated with 6*N*-methyl-alcoholic potassium hydroxide under conditions comparable with those used in the previous investigations of this series. The cooled product was mixed with an equal volume of absolute ethyl alcohol, and the insoluble salts were collected, washed with ethyl alcohol, drained, dissolved in the minimal amount of water, and decomposed with concentrated hydrochloric acid. The sparingly soluble acid thus obtained was crystallised from boiling water (100 parts), from which it separated in branched needles, m. p. 253° (decomp.)—a considerably higher m. p. than that recorded by Hell and Rempel (Found: C, 56·5; H, 5·9. Calc.: C, 56·5; H, 5·9%). The yield was 11% of the theoretical.

Oxidation of Suberocolic Acid.—On oxidation with alkaline permanganate, suberocolic acid gives (as it should) succinic and oxalic acids, but not in the expected yields. In one experiment, 0·8 g., on treatment with 140 c.c. of 3% permanganate (7 atoms of available oxygen), gave 0·5 g. of calcium oxalate (theory, 1·2 g.) and 0·3 g. of succinic acid (theory, 0·55 g.).

Reduction of Suberocolic Acid.—The acid (0·5 g.) was reduced with 30 g. of 4% sodium amalgam on the steam-bath during 3 hours. After the mercury had been removed, the solution was acidified and extracted with much ether.

Dihydrosuberocolic Acid (*A-form*).—The residue from the ether, after draining on porous porcelain, melted at 125—160°. After twice crystallising from water, small rosettes of needles were obtained, m. p. 170° (Found: C, 55·6; H, 7·0. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%). The acid instantly decolorises cold alkaline permanganate, and on vigorous reduction (see below) yields suberic acid.

Dihydrosuberocolic Acid (*B-form*).—This acid is formed along with suberic acid when suberocolic acid is reduced by boiling an aqueous solution with 50 g. of 4% sodium amalgam, added gradually during 4 hours. It separates from water in needles, m. p. 125° (Found: C, 55·7; H, 7·0%). The acid instantly decolorises cold alkaline permanganate, and on prolonged boiling with water and sodium amalgam yields suberic acid.

Suberic acid was separated from the B-form of dihydrosuberocolic acid by fractional crystallisation from hot water, and was identified by analysis (Found: C, 55·1; H, 8·0. Calc.: C, 55·2; H, 8·0%) and by comparison with a genuine specimen.

Δ^1-cyclo*Hexene*-1 : 2-*dicarboxylic Acid.*—The aqueous filtrate

from the suberocolic acid was extracted with ether, the residue obtained on evaporating the ether was rubbed with water, and the filtered solution evaporated in a vacuum. The residue obtained on evaporating the alcoholic solution with water was extracted with ether after acidification, and the residue from the concentrated and filtered ethereal solution was fractionally crystallised from ether. The combined residues were evaporated with water on the water-bath, and the crystals obtained after partial esterification of the residue were crystallised from water and identified by their properties, by analysis (Found: C, 56·3; H, 6·0. Calc.: C, 56·5; H, 5·9%), and by the m. p. of the anhydride (74°) prepared from them.

Δ^2-cyclo*Hexene*-1 : 2-*dicarboxylic Acid*.—The acids separated by means of water contained this *cyclo*hexene acid and suberocolic acid, which were separated by fractional crystallisation from water. The combined residues from the other ethereal and aqueous solutions were boiled with acetyl chloride for a short time, and the residue obtained by vacuum desiccation over potassium hydroxide was dissolved in ether and washed with sodium carbonate solution. The residue from the ether was dissolved in boiling water, from which the *cyclo*hexene acid (4·7%) was obtained in a pure condition by evaporation and three crystallisations from water. It was identified by its properties, by analysis (Found: C, 56·4; H, 6·0. Calc.: C, 56·5; H, 5·9%), and by conversion into the anhydride of the Δ^1-acid, as described by Baeyer (*loc. cit.*).

$\alpha\alpha'$-*Dimethoxysuberic Acid* (*A-form*).—The sodium carbonate washings, on acidification and extraction with ether, yielded a mixture of acids which was separated into two fractions by boiling with ether. The sparingly soluble portion crystallised from a small amount of water in leaflets or rosettes of small needles (yield 20·4%), m. p. 145—146° (Found: C, 51·0; H, 7·6. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7%).

$\alpha\alpha'$-*Dimethoxysuberic Acid* (*B-form*).—On subjecting the more soluble fraction to repeated fractional crystallisation, from ether and water alternately, a further quantity of A-acid was obtained, whilst the B-acid became concentrated in the mother-liquors, partly on account of its greater solubility, and partly because of its much slower speed of crystallisation. It was finally obtained (2·8%) as rosettes of needles, m. p. 117—118° (Found: C, 51·7; H, 7·6%).

Azelaic acid was prepared by the oxidation of ricinoleic acid, as described by Baker and Ingold (J., 1923, **123**, 128), and dibrominated in the form of its acid chloride. The dibromo-ester prepared from the dibromo-chloride was hydrolysed with 6*N*-methyl-alcoholic potassium hydroxide, as described in the earlier investigations of

this series. The acid product, a yellow syrup, was treated in various ways in the hope of inducing crystallisation, but without success, and it was therefore esterified with ethyl alcohol, and the ester carefully fractionated under reduced pressure, through a short column. After four distillations, the following fractions were obtained :

	(i).	(ii).	(iii).	(iv).	(v).	Residue.
B. p./30 mm. ...	198—205°	205—218°	218—221°	221—240°	240—260°	260°
Wt. (g.) ...	5·2	7·9	125·3	6·9	4·4	6·0
G./degree	0·7	0·6	41·8	0·4	0·2	—

αα'-Dimethoxyazelaic Acid (II).—The main fraction (iii), b. p. 218°/30 mm., on redistillation boiled mainly at 218—219°/30 mm. (Found : C, 58·9; H, 9·3. *Ethyl dimethoxyazelate*, $C_{15}H_{28}O_6$, requires C, 59·2; H, 9·2%). Both the main fraction and the central fraction gave on hydrolysis by hydrochloric acid a liquid mixture of the *meso*- and racemic forms of *αα'-dimethoxyazelaic acid* (Found : C, 52·8; H, 8·4. $C_{11}H_{20}O_6$ requires C, 53·2; H, 8·0%), which, even after purification through the *silver* salt (Found : Ag, 46·5. $C_{11}H_{18}O_6Ag_2$ requires Ag, 46·8%), could not be induced to solidify, and was therefore digested with thionyl chloride until sulphur dioxide ceased to be evolved. After the excess of thionyl chloride had been removed in a vacuum at 100°, the acid chloride was dissolved in ether and treated with dry ammonia; a crystalline precipitate, which, however, was a mixture of isomerides, was then obtained. Repeated crystallisation from water yielded one of the individuals in a pure condition as small plates, m. p. 164—165° (Found : C, 54·0; H, 8·6. $C_{11}H_{22}O_4N_2$ requires C, 53·7; H, 8·8%). The same *αα'-dimethoxyazelamide* was obtained by digesting the ester with aqueous ammonia (*d* 0·880) for a month. Stellate clusters of crystals were formed which, after two crystallisations from water and one from ethyl acetate, gave small plates identical with the above. The more soluble isomeride could not be isolated in a pure condition. Crystals of the correct composition, having m. p. 143—146°, were obtained, but as in the course of numerous crystallisations small amounts of the amide, m. p. 164—165°, were obtained from them, they were concluded to be a difficultly separable mixture.

αα'-Dihydroxyazelaic Acid (III).—Fractions (iv) and (v) obtained in the above preparation were combined with corresponding fractions in three similar experiments and fractionally distilled four times. *Ethyl αα'-dihydroxyazelate*, b. p. 235—240°/16 mm., was thus obtained (3·7 g.) (Found : C, 56·9; H, 8·9. $C_{13}H_{24}O_6$ requires C, 56·5; H, 8·7%). The *acid* obtained from it by hydrolysis with hydrochloric acid was a clear syrup which did not solidify, and from which no crystalline amide could be prepared (Found : C, 49·4; H, 7·7.

$C_9H_{16}O_6$ requires C, 49·1; H, 7·3%. Found for the *silver* salt: Ag, 49·7. $C_9H_{14}O_6Ag_2$ requires Ag, 50·2%).

α-Ketoazelaic Acid (VI).—Fractions (i) and (ii) obtained in the preceding preparations gave on hydrolysis with mineral acids a syrupy acid which instantly decolorised cold alkaline permanganate, but the only crystalline products which could be obtained from it had not this property. Fractional distillation of the esters yielded no fraction of constant boiling point, and treatment with ammonia gave an impure mixture of amides from which only the dimethoxyamide described above could be isolated. By hydrolysis of a fraction, b. p. 198—205°/23 mm., however, an acid was obtained which partly solidified after several months. On crystallisation from ether, rosettes of needles, m. p. 175°, were obtained (Found by microanalysis: C, 53·5, 53·7; H, 7·1, 7·1. $C_9H_{14}O_5$ requires C, 53·4; H, 7·0%). The amount obtained (0·05 g.) was insufficient for a detailed examination, but since the substance resembled α-ketoglutaric acid in giving a dull reddish-brown colour with ferric chloride, it is believed to be α-ketoazelaic acid, and not the isomeric hydroxy*cyclo*heptane acid.

We desire to record our thanks to the Royal Society for a grant with the aid of which some of the expense of this investigation has been defrayed.

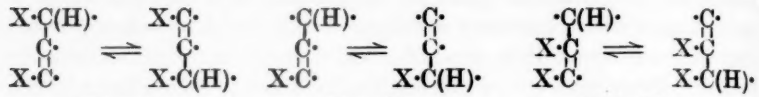
THE UNIVERSITY, LEEDS. [*Received, February 16th*, 1926.]

CXCIII.—*The Mechanism of Tautomeric Interchange and the Effect of Structure on Mobility and Equilibrium. Part I. The Three-carbon System.*

By CHRISTOPHER KELK INGOLD, CHARLES WILLIAM SHOPPEE, and JOCELYN FIELD THORPE.

IT has been shown (Birch, Kon, and Norris, J., 1923, **123**, 1361; Birch and Kon, *ibid.*, p. 2440; Kon and Linstead, J., 1925, **127**, 616, 815) that the mobility of the three-carbon system, which reaches a maximum in glutaconic esters (Type I), is also exhibited to a more limited degree in αβ- and βγ-unsaturated esters (Type II), in which only one terminal carbethoxyl group is present, and in analogous unsaturated ketones and nitriles. This paper deals with the general question of the influence of substituents on tautomeric mobility, and includes a study of the case in which,

in addition to one terminal carbethoxyl group, a second carbethoxyl group is attached to the central atom of the three-carbon system (Type III).

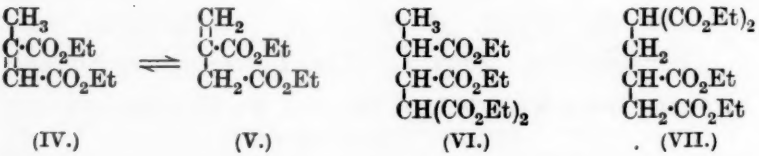


(Type I.) (Type II.) (Type III.)

$X = CO_2Et$

A noteworthy contrast between systems (I) and (II) is that, whilst compounds of type (I) (glutaconic esters) usually attain equilibrium in the absence of an added reagent so that the isomeric forms cannot be isolated as distinct individuals, substances belonging to type (II) frequently require the addition of an alkaline catalyst, such as alcoholic sodium ethoxide, to bring about interconversion of the forms. Type III is found to resemble type II in this respect; on the other hand, there are important differences between these two types in the general character of the equilibria to which they attain.

Citraconic and itaconic esters (IV and V) belong to type III, and they can, of course, be obtained as distinct individuals. There are, however, definite indications of their interconvertibility in the presence of alcoholic sodium ethoxide. Thus Hope found (J., 1912, **101**, 894) that if citraconic ester were treated with ethyl sodiomalonate in ether or benzene, the normal addition compound (VI) was formed; whereas if he used alcohol as solvent, an isomeric ester (VII) was obtained, which could also be prepared directly from itaconic ester.



(IV.) (V.) (VI.) (VII.)

A re-examination of this reaction has shown that *both* the ester (VI) and its isomeride (VII) are formed from either citraconic or itaconic ester under a considerable variety of conditions, *e.g.*, by treatment with an equivalent or a large excess of sodium ethoxide in cold or in hot ethyl alcohol, or with sodium in boiling benzene. Under other conditions, only one isomeride could actually be isolated in the pure condition, the formation of the other being established by the production of derivatives.

These experiments, a fuller account of which is given below,

strongly emphasise the suggestion that citraconic and itaconic esters are tautomeric in the presence of sodium ethoxide, just as are the esters (and nitriles, etc.) of type II previously discussed. Hope, however, advanced the opinion that the interconversion in the presence of sodium ethoxide might take place through the adding on and splitting off of alcohol in accordance with the following scheme, and he succeeded in isolating an ethoxy-derivative to which formula (VIII) was assigned.

(IV.) $\rightleftharpoons$ $CH_3 \cdot C(OEt)(CO_2Et) \cdot CH_2 \cdot CO_2Et$ (VIII.) $\rightleftharpoons$ (V.)

This view has, of course, the same mechanical simplicity as other "adding on and splitting off" theories of isomeric change, and it is necessary to explain why we regarded it as improbable. First it has been shown (E. H. Ingold, J., 1925, **127**, 469) that although, in reversible addition reactions, fission corresponding with addition in the direction favoured by polar influences is in general readily effected, yet fission corresponding with addition in a non-favoured direction takes place with difficulty or not at all. The conversion of (VIII) into (V), involving as it does the removal of a β-ethoxyl group along with an α-hydrogen atom, would be a fission of the latter class, and would certainly not take place under the experimental conditions employed. Secondly, in all alcohol-additions to unsaturated esters, the ethoxyl group takes up the same position as does the $-CH(CO_2Et)_2$ group in the corresponding additions of ethyl malonate. Hence, regarding the malonic ester addition products (VI) and (VII) as derived from (IV) and (V), respectively, we see that if citraconic ester formed an ethoxy-compound it should have formula (IX), whilst if itaconic ester gave one it should have formula (X); and either of these on losing alcohol would, of course, pass back into the ester from which it was derived. Thus, not only would an ester of constitution (VIII) not be formed, but, even if it were, it would not undergo the changes which it was invented to explain.

$CH_3 \cdot CH(CO_2Et) \cdot CH(OEt) \cdot CO_2Et$ (IX.) $\quad$ $OEt \cdot CH_2 \cdot CH(CO_2Et) \cdot CH_2 \cdot CO_2Et$ (X.)

Proof that Hope's ethoxy-ester has in reality formula (X) was obtained by converting the corresponding ethoxy-acid (XI) with hydrobromic and hydriodic acids into the bromo-acid (XII) and the iodo-acid (XIII), respectively, and into the lactone (paraconic acid) of the hydroxy-acid (XIV), all of which were identified by comparison with specimens synthesised for the purpose. The isomeric bromo- and hydroxy-acids corresponding with the ethoxy-esters (VIII) and (IX) are known and their m. p.'s and properties

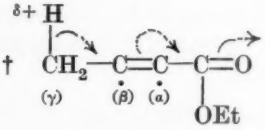
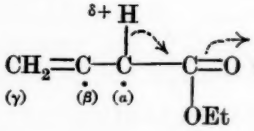
are such that they could not be confused with the substances obtained.*

$OEt\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$ (XI.) $\quad CH_2Br\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$ (XII.)

$CH_2I\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$ (XIII.) $\quad OH\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$ (XIV.)

Thus, there is no evidence that an ethoxy-ester intervenes in the conversion of citraconic ester into itaconic ester; on the contrary, itaconic ester obviously must intervene in the conversion of citraconic ester into the ethoxy-ester obtained; and, naturally, the same ethoxy-ester can be obtained from itaconic ester directly.

Our view of the effect of sodium ethoxide and other alkaline reagents in promoting the interconversion of these and the other three-carbon tautomerides is best made clear by reference to a recent paper by Holmes and Ingold (this vol., p. 1305), in which it is shown that a hydrogen atom attached to a hydrocarbon radical may be extracted in the form of its ion (that is, the nucleus only) by the action of a powerful negative ion such as hydroxyl, and that this process is facilitated if the hydrogen atom is already in a state of *incipient* ionisation owing to the presence in the molecule of a group (electron-sink) which exerts a pull on the electrons involved in binding the hydrogen atom. Now the carbethoxyl group, like all groups which are *m*-directive in aromatic substitution, is regarded as a powerful electron-sink (compare Allen, Oxford, Robinson, and Smith, this vol., p. 401; Ingold and Ingold, *ibid.*, p. 1310), and hence the "mobile hydrogen atom" in citraconic and itaconic ester, and in similar pairs of three-carbon tautomerides, may be assumed to be in a state of incipient ionisation owing to small electron displacements in the directions

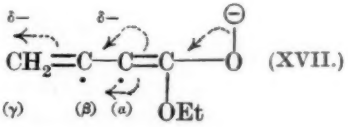
(XV.)†  and  (XVI.)†

The former scheme is precisely similar to that given by Ingold and Ingold for *m*-substitution in the benzene ring (*loc. cit.*, Case 2, p. 1312). The conditions under which the isomeric change may occur will now depend entirely on the extent to which this preliminary loosening of the potential hydrogen ion has taken place.

* Dr. Hope, to whom these data were privately communicated, is in complete agreement with the structural conclusions.

† For explanation of symbols, see Ingold and Ingold, *loc. cit.*, p. 1312, footnote.

If incipient ionisation is considerable, mere loose combination with neutral solvent molecules (ordinary hydrion solvation) will be sufficient to draw the hydrogen nucleus away. If, on the other hand, it is slight, the more powerful attraction of a negative ion will be required to effect removal, and it is in this way, we believe, that sodium ethoxide, a source of negative ethoxyl ions, acts in facilitating the interconversion of three-carbon tautomerides. As the hydrogen nucleus is drawn away, so the electron displacements, originally minute, are enabled to progress in the sense of formulæ (XV) and (XVI), until, when ionic dissociation is complete, the displacement also is complete, the negative ionic charge appearing on the oxygen atom; thus (XV) and (XVI) give the common ion (XVII).



(XVII.)

The second half of the process, the recombination of the negative ion (XVII) with hydrion, is similarly comparable with *op*-substitution, the ion (XVII) corresponding in structure with a phenoxide ion (*loc. cit.*, Case 1, p. 1312). In each of these ions there is assumed to be a weak tendency towards a return of the electrons, giving (in different electromeric phases) small negative charges in the α- and γ- (or *o*- and *p*-) positions, to which, therefore, either positive ions, or the positive ends of incipiently ionised molecules, become attracted. In the case now under consideration, the positive ions would be solvated hydrions, and as combination proceeds, so the electrons would be drawn back in the sense of formula (XVII) until either the neutral molecule (XV) or its isomeride (XVI) is regenerated (compare with diazo-coupling).* Or, an incipiently ionised molecule, such as water or alcohol, may be attracted, and the positive end of it (hydrogen) transferred to the three-carbon system by reaction in a cycle (compare with *op*-nitration, *loc. cit.*).

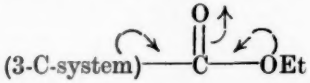
This view of activation in tautomeric change represents a rational development of principles previously formulated by E. H. Ingold (*Chem. and Ind.*, 1923, **42**, 1246),† and we would apply it not only

* The hydrions will, of course, also approach and combine with the negatively charged oxygen atom, but this produces no new isolable isomeride and is easily reversible (ordinary ionic dissociation). It is the circumstance that, when the hydrion approaches C_α or C_γ the electrons return along the chain to that point and so *bind* the hydrion, which (according to this view) gives to the αβ- and βγ-unsaturated isomerides their stability as individuals.

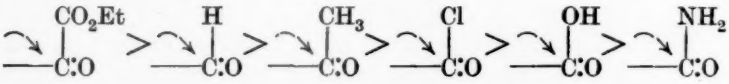
† Read to Section B of the British Association at Liverpool, September, 1923.

to three-carbon tautomerism, but also, with appropriate modifications, to all other mobile-hydrogen tautomeric systems, including ring-chain systems. Illustrations of its applications are, however, now confined to certain effects of structure on three-carbon tautomerism.

The effect of the terminal groups on the *mobility* of the three-carbon system (compare *inter alia*, Ingold and Piggott, J., 1922, **121**, 2381; Birch, Kon, and Norris, *loc. cit.*) may readily be correlated with directive action in benzene substitution. Thus the smaller mobility of systems terminated by a carbethoxyl or carboxyl group, as compared with similar systems terminated by an acetyl group, is regarded as due to the competition :



This is only a particular case of the general principle that the greater the electron-giving tendency possessed by a group R (as indicated by its *op*-directive power in aromatic substitution) the smaller will be the mobility of a three-carbon system terminated by ·CO·R. Thus the sequence $NH_2>OH>Cl>CH_3>H>CO_2Et$ for *op*-directive power leads to the sequence

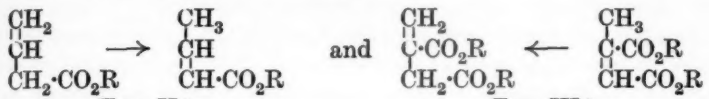


for the enhancement of three-carbon mobility. Similar series apply to related phenomena discussed by E. H. Ingold (*loc. cit.*) and, in passing, it may be noticed that the difference –CO·Cl>–CO·OH is utilised in the Hell-Volhard method of brominating aliphatic acids through their chlorides. The reason for the greater mobility of three-carbon systems in which there are two terminal carbethoxyl groups (glutaconic esters, type I) as compared with those in which there is only one (types II and III) is too obvious to require elaboration.

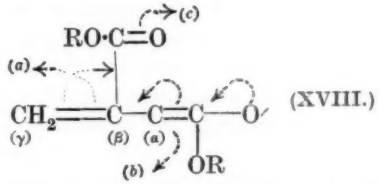
A general discussion of the effect of groups on the three-carbon *equilibrium* would necessarily be lengthy, but the method of treatment can be illustrated by means of a few examples. In the simple case of a three-carbon system activated by one terminal group, say a carboxyl group, six types of modification by substitution are possible, since either an *op*-directive group (electron source) or a *m*-directive group (electron-sink) might be introduced into either the α-, or the β-, or the γ-position.

As illustration, we may consider the introduction of an electron sink into the β-position, the effect of which is to displace the

equilibrium in the direction favouring the $\beta\gamma$-unsaturated isomeride. For example, the isomeric changes



form a striking contrast (compare also Baeyer, *Annalen*, 1890, **258**, 165; Hassell and Ingold, this vol., p. 1465; Goss and Ingold, *ibid.*, p. 1471). The reason for this effect is clearly seen if we consider the return of the electrons in the ion (XVII). Two routes are originally open, (*a*) and (*b*) (XVIII), but one of these (*a*) clashes with path (*c*) provided by the β-group; hence the hydrogen ion combines preferentially at the α-carbon atom:



(XVIII.)

Similarly, in aromatic substitution, the introduction of a *m*-directing group in the *m*-position to a powerful *op*-directing group tends to facilitate substitution in the position *between* the two groups.

Again, the introduction of an *op*-directing group (electron source) in the γ-position will oppose (*a*), and in the absence of disturbing factors should therefore favour the $\beta\gamma$-unsaturated isomeride. γ-Alkyl groups are known to have this effect (compare *inter alia*, Wallach, *Annalen*, 1912, **394**, 376; Beesley, Ingold, and Thorpe, J., 1915, **107**, 1080; Birch, Kon, and Norris, *loc. cit.*; Kon and Linstead, *loc. cit.*). Analogous considerations may be applied to other cases, and the comparison with aromatic substitution obviously gives great scope for the prediction of the relative magnitude as well as the direction of the effect to be expected from different substitutions in different positions.

The analogy between tautomerism and reversible additive reactions has been emphasised in a number of recent memoirs, and a discussion of the application of these views to that subject will be given in an ensuing paper.

Experimental.

Citraconic anhydride was obtained (3 kg.) from citric acid, and the fraction, b. p. 204—205°/760 mm., esterified as described by Hope. It is important to distil the anhydride under ordinary

pressure to isomerise any itaconic anhydride. The ethyl citraconate had b. p. 118—120°/20 mm. (yield, 80%). Ethyl itaconate, b. p. 119—120°/20 mm., was prepared from itaconic acid.

Addition of Ethyl Sodiomalonate to Ethyl Citraconate and Ethyl Itaconate and Separation of the Products.—Ethyl sodiomalonate was prepared in the usual manner, with ethyl alcohol as solvent and the theoretical quantity of sodium, and the ethyl citraconate (1 mol.) added, the temperature being kept at 15°. After 24 hours, the pale yellow product was poured into water, and the product extracted with ether and washed with sodium carbonate. The residue obtained on evaporation of the ether was subjected to a long series of fractional distillations, as a result of which it was partly separated into two products: (*a*) b. p. 198—199°/10 mm., and (*b*) b. p. 190—191°/10 mm. The former (*a*) was ethyl *n*-butane-αβδδ-tetracarboxylate, since on hydrolysis by hydrochloric acid it gave *n*-butane-αβδ-tricarboxylic acid, m. p. 121°, which was identified by comparison with a specimen prepared by hydrolysing the product of condensing ethyl sodioethanetricarboxylate with ethyl β-iodopropionate. The fraction (*b*) consisted of ethyl *n*-butane-αaβγ-tetracarboxylate, since on hydrolysis it gave *trans*-α-methyltricarballylic acid, m. p. 185°.

In view of the unsatisfactory character of this separation, the crude product obtained from the condensation of 525 g. of citraconic ester and 455 g. of ethyl malonate was treated in the following manner. An ethereal solution was shaken with 2*N*-aqueous sodium hydroxide and then mixed with 100 c.c. of ice-water and 50 c.c. of 50% potassium hydroxide. This alkaline solution was extracted twice with ether, the combined ethereal extracts were evaporated, and the residue was fractionally distilled. A first fraction (8 g.) had b. p. 140—180°/12 mm., and the main fraction (22 g.) b. p. 180—192°/12 mm.; on redistillation, this gave a colourless oil (20 g.), b. p. 189—190°/11 mm., consisting of ethyl *n*-butane-αaβγ-tetracarboxylate (Found: C, 55·5; H, 7·5. Calc.: C, 55·5; H, 7·5%), since it yielded *n*-butane-αβγ-tricarboxylic acid on hydrolysis. The potassium hydroxide solution was acidified and extracted with ether, and the extract washed thoroughly with saturated aqueous sodium hydrogen carbonate. On evaporation of the extract, an oil (15 g.) was obtained, which on distillation gave a fraction (6·5 g.), b. p. 205—210°/15 mm., consisting of ethyl *cyclo*pentan-3-one-1 : 2 : 4-tricarboxylate. On boiling this with hydrochloric acid for one hour and evaporating the solution, *cyclo*-pentanone-3-carboxylic acid, m. p. 62—64°, b. p. 170—174°/17 mm., was obtained. The more volatile ester fraction (5 g.), b. p. below 200°/15 mm., contained the ethyl *cyclo*pentanonedicarboxylate and

ethyl *cyclo*pentanonecarboxylate described below. The sodium hydrogen carbonate solution was acidified with hydrochloric acid and extracted with ether, and the residue (60 g.) from the extract esterified with ethyl alcohol and sulphuric acid in the usual manner. An ethereal solution of the esters so obtained was washed with aqueous sodium hydrogen carbonate and then with aqueous potassium hydroxide at 0°. The ester (20 g.) on fractional distillation gave 12 g. of an oil, b. p. 200—204°/12 mm., consisting of ethyl *n*-butane-αβδδ-tetracarboxylate (Found: C, 54·7; N, 7·4. Calc.: C, 55·5; H, 7·5%), since on hydrolysis only *n*-butane-αβδ-tricarboxylic acid was obtained. The sodium hydroxide solution was acidified with hydrochloric acid and extracted with ether, and the extract washed with aqueous sodium hydrogen carbonate and then with ice-cold 10% aqueous potassium hydroxide. The ether extract on evaporation gave a resin. The potassium hydroxide solution was acidified and extracted with ether; ethyl *cyclo*pentanone-1:2:4-tricarboxylate was then obtained. The sodium hydrogen carbonate solution was reacidified with hydrochloric acid, and the product obtained on extraction with ether was esterified with alcohol and sulphuric acid. The esters, after being washed in ethereal solution with aqueous sodium hydroxide and distilled, yielded, in addition to a small amount of substance, b. p. below 140°, a main fraction, b. p. 210—245°/12 mm., consisting essentially of ethyl dicarboxy*cyclo*pentenylmalonate (see below). The sodium hydroxide solution was treated at 0° with excess of carbon dioxide, and the oil thus precipitated was extracted with ether. The residue from the ether on distillation gave a small fraction, b. p. below 145°/12 mm., and a main fraction, b. p. 145—154°/12 mm., consisting of ethyl *cyclo*pentanonedicarboxylate (see below). The carbonated solution was rendered acid, and the product extracted with ether and re-esterified with alcohol and sulphuric acid. The esters so obtained, after being washed in ethereal solution with alkali and distilled, gave principally a fraction, b. p. 230—240°/12 mm., consisting mainly of ethyl dicarboxy*cyclo*pentenylmalonate.

The various "low" fractions mentioned in the course of the foregoing account were combined and examined. They consisted principally of unaltered ethyl malonate, ethyl mesaconate, and ethyl itaconate, a possible indication of the reversibility of the reaction.

The same nine substances, namely, ethyl malonate, itaconate, mesaconate, butane-ααβγ-tetracarboxylate, butane-αβδδ-tetracarboxylate, *cyclo*pentanone-mono-, -di-, and -tri-carboxylate, and dicarboxy*cyclo*pentenylmalonate, were obtained, by the same method of separation, when the original condensation was carried

out at 80°, and also when ethyl itaconate was substituted for ethyl citraconate in either experiment. Similar condensations carried out with itaconic and with citraconic ester, both at 15° and at 80°, with the difference that the quantity of sodium employed was twice the theoretical, yielded the same products, together with a pale yellow mixture of sodium compounds the nature of which has not yet been elucidated. Other condensations were carried out in boiling benzene as the solvent, the ethyl sodiomalonate being prepared from "molecular" sodium and ethyl malonate. When ethyl citraconate was used, not only ethyl butane-$\alpha\alpha\beta\gamma$-tetracarboxylate, but also $\alpha\beta\delta\delta$-tetracarboxylate and the *cyclo*pentane-esters were obtained. The use of excess of sodium made no difference to these results, and the yellow sodium compounds were not obtained as when alcohol was used as solvent. Other condensations were effected by the aid of molecular sodium (1 mol.) in dry ether. In this case, using ethyl citraconate, ethyl butane-$\alpha\alpha\beta\gamma$-tetracarboxylate was obtained in 80% yield, and the $\alpha\beta\delta\delta$-ester was not isolated; but it must have intervened in the production of ethyl *cyclo*pentanonetricarboxylate, which was identified by hydrolysis to *cyclo*pentane-3-carboxylic acid, m. p. 62°. The use of excess of sodium did not affect this result. Similar experiments using ethyl itaconate in place of ethyl citraconate led to 65—75% yields of ethyl *n*-butane-$\alpha\beta\delta\delta$-tetracarboxylate, which was identified through its amide (m. p. 255°; compare Michael and Schulthess, *J. pr. Chem.*, 1892, **45**, 57) and hydrolysis product. The *cyclo*pentane esters were also obtained, but ethyl *n*-butane-$\alpha\alpha\beta\gamma$-tetracarboxylate could not be identified. The presence of excess of sodium did not affect this result.

It appears, therefore, that the mobility of the unsaturated esters is less in benzene and ether than in alcoholic sodium ethoxide, and that in ether particularly, possibly on account of its low b. p., there is very little interchange.

The following compounds are new.

Ethyl cyclo*pentanone*-3-*carboxylate* is a colourless oil, b. p. 109—111°/10 mm. It gives no colour with ferric chloride (Found: C, 61·4; H, 7·7. $C_8H_{12}O_3$ requires C, 61·5; H, 7·7%). The *semicarbazone* was prepared by means of semicarbazide acetate and crystallised from ethyl alcohol in needles, m. p. 153·5° (Found: C, 50·6; H, 7·2. $C_9H_{15}O_3N_3$ requires C, 50·7; H, 7·0%). The ester can be prepared by way of the acid chloride, which is obtained when phosphorus pentachloride acts on *cyclo*pentanone-3-carboxylic acid.

Ethyl cyclo*pentanone*-2 : 4 (*or* 2 : 3)-*dicarboxylate* has b. p. 150°/10 mm. and 160°/18 mm. It gives a deep red colour with ferric chloride (Found: C, 57·6; H, 7·3. $C_{11}H_{20}O_5$ requires C, 57·8;

H, 7·0%). A semicarbazide could not be prepared. On hydrolysing the ester with hydrochloric acid, *cyclo*pentanonecarboxylic acid, m. p. 64°, was obtained.

Ethyl 2 : 4 (*or* 2 : 3)-*Dicarboxy*cyclo*pentenylmalonate* (*or Ethyl* 2 : 4 [*or* 2 : 3]-*dicarboxy*cyclo*pentylidenemalonate*).—A number of crude specimens of this ester (51 g.) were combined and carefully distilled; 43 g. of a pure fraction, b. p. 240—245°/16 mm., were then obtained (Found: C, 58·3; H, 7·1. $C_{18}H_{26}O_8$ requires C, 58·3; H, 7·1%). The ester was unsaturated and gave no colour with ferric chloride. It showed an exaltation of refractivity of 1·9 units for sodium light ($n_D^{21°}$ 1·46719; *d* 1·13273). The acid obtained on hydrolysis was a syrup, and may have been a mixture of the endocyclic and exocyclic unsaturated acids, since the parent ester would almost certainly be tautomeric. From the first fractions obtained in the distillation of the above ester, a semicarbazone was obtained which was identified with that described above, m. p. 153·5°.

Formation and Constitution of Ethyl ω-Ethoxymethylsuccinate.—This ester may be prepared either from citraconic ester, as described by Hope, or from itaconic ester. Using Hope's method, we found some difficulty in obtaining the ethoxy-ester free from unsaturated esters, but after a series of careful fractionations, about 15—20% of an ester, b. p. 137—140°/23 mm., was obtained which decolorised permanganate only slowly. It gave correct figures on analysis and on treatment with aqueous ammonia yielded *ω-ethoxymethylsuccinamide*, which was isolated by evaporating the ammonia solution in a vacuum and crystallising the residue from water. Thus obtained, the amide formed prisms, m. p. 149—150° (Found: C, 48·4; H, 7·8. $C_7H_{14}O_3N_2$ requires C, 48·3; H, 8·0%). By the use of itaconic ester (20 g.), sodium (0·16 g.), and alcohol (96 c.c.), and by keeping the mixture at the ordinary temperature overnight, a product was obtained which, after four fractional distillations, yielded 3 g. of an unsaturated ester, b. p. 130—135°/23 mm., and 5 g. of an ester, b. p. 137—140°/23 mm., which only slowly decolorised alkaline permanganate. The unsaturated ester, on treatment with ammonia, was converted into mesaconamide, m. p. 176—177° (Found: C, 47·0; H, 6·3. Calc.: C, 46·9; H, 6·2%) and must therefore have consisted largely of mesaconic ester. The saturated ester was evidently the same ethoxy-ester as that obtained from citraconic ester, since it gave the same amide, m. p. 149—150°, on treatment with ammonia and the same acid on hydrolysis (Found: C, 56·6; H, 8·6. Calc.: C, 56·9; H, 8·6%). The ethoxy-acid obtained on hydrolysis had the m. p. and properties described by Hope.

α-Iodopropane-βγ-dicarboxylic Acid.—The ethoxy-acid (2 g.) was boiled for 2 hours with "Zeisel" hydriodic acid, and the ethyl iodide formed allowed to escape. The resulting solution was extracted with ether, and the extract washed with thiosulphate solution, dried, and evaporated. The residue immediately solidified with evolution of heat, and after crystallisation from ethyl acetate–ligroin had m. p. 138° (Found : C, 23·9; H, 2·7. Calc. : C, 23·2; H, 2·7%). It was identified by direct comparison and a mixed m. p. determination with a specimen of α-iodopropane-βγ-dicarboxylic acid prepared for the purpose.

α-Bromopropane-βγ-dicarboxylic Acid.—The ethoxy-acid was boiled for 3 hours with hydrobromic acid (*d* 1·49), and the product extracted with ether. The residue obtained at once solidified, and after crystallisation from ethyl acetate–petrol had m. p. 137°. It was identified by the m. p. of a mixture with a genuine specimen.

Paraconic Acid.—Both the iodo- and the bromo-acid were treated with excess of silver oxide in aqueous suspension; heat was generated and the silver halide precipitated. The acid extracted with ether after addition of mineral acid solidified in an evacuated desiccator and then melted at 50—53°. After crystallisation from ether–chloroform, paraconic acid was obtained, m. p. 57°, and identified by direct comparison and a mixed m. p. determination with an authentic specimen.

We take this opportunity to record our thanks to both the Chemical Society and the Royal Society for grants with the aid of which the cost of this investigation has been defrayed.

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CXCIV.—*The Constitution of Polysaccharides. Part IX. The Degradation of Cellulose to an Anhydrotrisaccharide.*

By JAMES COLQUHOUN IRVINE and GEORGE JAMES ROBERTSON.

IN former papers from this laboratory it was shown that cotton cellulose is composed of 1 : 5-anhydroglucose residues * and the question was discussed as to the number of such residues present in the unpolymerised molecule of the polysaccharide. It was

* See Appendix for discussion and revision of numerical nomenclature as applied throughout this paper.

pointed out (Irvine and Hirst, J., 1923, **123**, 518) that the simplest view which satisfies the primary conditions is that cellulose is a polymerised di(1 : 5-anhydroglucose) (*loc. cit.*, p. 524, Formula IV) but that a formula of this type is at variance with the highest authentic yield of cellobiose octa-acetate so far obtained from a normal cellulose. In order to accommodate this result and yet preserve the greatest simplicity of structure, it was suggested that cellulose may be regarded as a polymeride of tri-1 : 5-anhydroglucose. The suggestion was tentative, as shown by the following significant extract from the argument :—"*in the meantime it is prudent to select a formula for cellulose which will give a yield of cellobiose approximating to this figure* (50—60%) *rather than to the higher value* 105·5." The same reasonable caution has been exercised in our other references to this question, but nevertheless the views expressed have been generally invested with a rigidity and finality for which no claim was made. The present position is that the exact number of anhydroglucose residues which form the cellulose molecule remains unknown and speculation regarding this factor must be guided from time to time as knowledge accumulates. Recently, *X*-ray spectrographic methods have been brought to bear on the problem and the results are interpreted as indicating that the C_6 residues are marshalled in even numbers. This conclusion is opposed to the idea that the molecular unit is an anhydro-trisaccharide, but the results of standard chemical methods of attacking constitutional questions must equally be taken into account, even if, for the time being, they conflict with data obtained by purely physical processes. Obviously, the anhydro-trisaccharide formula need no longer be considered if convincing chemical evidence is forthcoming that the cellulose molecule is of a single type and definitely contains an even number of C_6 residues. But it will be generally agreed that the acceptance of any particular molecular formula must rest ultimately on the depolymerisation of cellulose to the simplest non-reducing compound possessing the empirical formula $C_6H_{10}O_5$ and retaining the 1 : 5-anhydro-linking. Further, such a compound should be capable of undergoing the reverse change of polymerisation without disturbance of the characteristic 1 : 5-anhydride ring and without forming complex glucosides of the type produced by the polymerisation of glucosan (Irvine and Oldham, J., 1925, **127**, 2903). This prospect is still remote, but we now submit experimental evidence, bearing on the problem, which has been obtained by studying the graded acetolysis of cotton cellulose.

A review of the scattered literature and more particularly of papers which have appeared in the past few years reveals that acetolysis is an extremely complex process and is not confined to a

succession of reactions conducted on cellulose triacetate. Much recent work rightly emphasises the esterifying effect of the sulphuric acid employed in acetolysis, but nevertheless the earlier researches of Klein and of Schliemann reveal the essential nature of the changes involved. These workers showed that even when the yield of cellulose octa-acetate is as much as 60% of the cellulose used, degradation products persist which may be regarded as simple dextrins and possess a greater complexity than a disaccharide. These dextrin acetates are dextrorotatory and appear to be the immediate precursors of cellobiose octa-acetate, so that acetolysis may be regarded as a series of ill-defined steps as represented below. The scheme does not include the formation of aceto-sulphates as, from the point of view of the present investigation, these products arise from secondary reactions, and as cellulose has been completely converted into 2 : 3 : 6-trimethyl glucose, it is also unnecessary to make separate provision for *iso*cellobiose acetate.

Cellulose → Acetylated cellulose → Acetylated cellulose dextrins →
[X] → Cellobiose octa-acetate → Glucose penta-acetate.

Acetylation and depolymerisation are the essential features of the earlier reactions, and the opening of anhydro-rings by hydrolysis is specially characteristic of the two final stages, but there is no sharp line of demarkation between these different types of change. The hypothetical stage indexed as [X] therefore represents the formation of compounds in which the maximum depolymerisation of cellulose has taken place, whilst the specific hydrolytic action responsible for the formation of cellobiose octa-acetate is a minimum. The present investigation deals with the exploration of this group of acetolysis products.

Several workers, notably Bertrand, Hess, and Pringsheim, have occupied themselves with what is essentially the same subject of research and have obtained results of great interest. It is, however, a difficult matter to define exactly the experimental conditions under which acetolysis can be controlled so as to give consistent results. The physical condition of the cellulose used and the treatment to which it has been subjected, minute variations in the purity of the reagents employed, the temperature and other factors still unrecognised, combine to affect the series of reactions profoundly. In consequence, through no fault of the observers, the statements in the literature are occasionally conflicting. We find, however, that the progress of acetolysis can be ascertained by systematic physical examination of samples of the product and that it is possible to arrest the reactions at a stage immediately before cellobiose octa-acetate is formed and when insoluble dextrins are

present in minimum amount. This result was secured by working between two limiting conditions, the first being that no trace of crystalline structure should be observable in the solid product when examined by ordinary microscopic methods. Control experiments showed that as small a proportion as 3% of cellobiose octa-acetate can be identified with certainty in this way. The second limiting condition was that a solution of the product in chloroform should be dextrorotatory and should show only a faint cone of light when viewed in the ultramicroscope. This secured that insoluble dextrins constituted less than 7% of the total. The product obtained when these conditions were preserved was a white amorphous powder and the composition was that of a cellulose triacetate, but its properties presented a sharp contrast with those of a normal acetate of the polysaccharide. In particular, it displayed a much wider range of true solubility, possessed a distinct, although indefinite, melting point, and was dextrorotatory. The change of sign from the lævorotation characteristic of cellulose triacetate is in itself proof that extensive depolymerisation had taken place. Despite the uniformity in properties and composition displayed by different preparations, the product was a mixture and contained at least two constituents which reduced Fehling's solution, the ratio of the cuprous oxide formed before and after acid hydrolysis being 1 : 2·2. The greatest caution must be exercised in interpreting all analytical data in the case of acetolysis products and consequently the nature of the degraded acetate was ascertained by submitting it to (1) deacetylation and (2) methylation. Treatment with aqueous dimethylamine eliminated the acetyl groups and enabled dextrins to be removed. The main product thus obtained was freely soluble in water but, owing to secondary reactions between reducing groups and the alkaline reagent (Irvine, Thomson, and Garrett, J., 1913, **103**, 238), the material was contaminated with alkylamino-derivatives and could not be completely separated into its constituents. This section of our work is being continued, but it may be stated that we have isolated from the above mixture an amorphous disaccharide which was present to the extent of about 20%. The sugar melted with decomposition at 180°, and had $[\alpha]_D + 14°$ in water, but until this extension of the research is complete it is impossible to characterise the compound definitely as an *iso*cellobiose.

These experimental difficulties were overcome by submitting the mixture of degradation compounds to the methylation process, which was adjusted so as to eliminate both alkylated disaccharides and dextrins. Contrasted with the behaviour of cellulose under parallel conditions, the methylation proceeded with remarkable smoothness and no difficulty was experienced in obtaining the fully

substituted derivative, a result which supplies additional evidence that extensive depolymerisation of the polysaccharide had been accomplished. As only the material insoluble in sodium hydroxide was collected, any disaccharide or monosaccharide constituents were retained in the alkaline liquors and were thus eliminated. Methylated dextrins, amounting to 6% of the total weight, were left undissolved on treatment with ether, so that, so far as molecular complexity is concerned, the product finally isolated was intermediate between lower dextrins and disaccharides. In this way, a 50% yield of a white, amorphous powder was obtained which was readily soluble in organic solvents, and possessed the properties of a glucoside. Molecular-weight determinations by the cryoscopic method in benzene solution, and confirmed by Rast's process, gave the value 656, showing that the substance was derived from a trisaccharide. The analytical composition also corresponded exactly with that required for $[C_6H_7O_2(OMe)_3]_3$ and the combined results might well have been accepted at this stage as conclusive. The behaviour on hydrolysis, however, warrants the conclusion that only 70% of the material consisted of tri(trimethyl anhydroglucose), the remainder being the corresponding methylated trisaccharide. This evidence was obtained by heating with acid methyl alcohol, which effected hydrolysis and the condensation of the liberated sugars with the solvent. The product of this reaction was isolated by vacuum distillation and consisted of a mixture of trimethyl methylglucoside (90%) with tetramethyl methylglucoside (10%). This opinion was verified in two ways. The mixture of glucosides was hydrolysed and the sugars thus obtained consisted exclusively of 2 : 3 : 6-trimethyl glucose and 2 : 3 : 5 : 6-tetramethyl glucose, both of which were isolated in crystalline form in yields which correspond with the above composition. Further, precisely the same result was obtained when the original methylated product was hydrolysed by means of aqueous acid to give the corresponding sugars directly without the intermediate formation of the glucosides. The combined evidence leads to the opinion that, under the conditions specified, cellulose can be degraded to a mixture of acetates derived from the following compounds in the proportions stated :—

1. Dextrins	6%	3. Triglucose	15%
2. Anhydro-triglucose	35%	4. Diglucose	20%

Although the results clearly favour the idea that anhydro-triglucose forms part of the cellulose aggregate, the possibility remains that anhydro-diglucose molecules may also be concerned in the polymerisation which leads to the polysaccharide. This possibility has been foreshadowed by the work of Irvine and Oldham (*loc. cit.*), who showed that the polymerisation of β-glucosan

involves both odd and even numbers of the monomeric unit, and is emphasised by consideration of the yields of the various products obtained in the present research. Although our work was carried out under conditions as nearly as possible quantitative, only 76% of the degraded acetates was accounted for in the form of pure derivatives. Further, during the original acetolysis, about 30% of the cellulose was converted into soluble or volatile products. Making allowance for these factors, it follows that the yield of trisaccharide derivatives actually obtained by us is of the order 35% when referred to the weight of cellulose originally employed. This is a minimum value and there seems no reason for doubt that at least one-third of the polysaccharide is based upon the triglucose unit. The remaining two-thirds of the polymerised aggregate remains unknown and the research is consequently being continued on the following lines: (1) the constitutional study of the tri- and di-saccharide products of graded acetolysis, (2) the polymerisation of these products and (3) the quantitative relationship between the tri- and di-saccharides.

Discussion of Results.

The views expressed in the present paper depend on the conversion of cellulose into simple methylated compounds, one of which is derived from triglucose and one from the corresponding anhydro-triglucose. Although it was possible to separate these two constituents from other compounds, it proved impossible to separate them from each other and thus the conclusions are in part based upon analytical figures. This in itself would be insufficient, but although there is ample supplementary evidence, it is necessary to discuss the results critically and to consider in how far explanations other than that offered are valid. Much depends on the fact that tetramethyl glucose is formed as a scission product when the above methylated mixture is hydrolysed, and the obvious suggestion is that the small amount of this sugar which was isolated may be traced to glucose penta-acetate or to cellobiose octa-acetate present in the original starting material. This possibility is discounted by the fact that the degraded acetates were amorphous, although this observation does not exclude the presence of an *iso*cellobiose acetate. Of greater importance is the technique employed in the methylation which, on the basis of control experiments, was adjusted so as to eliminate both mono- and di-saccharides.

It is therefore evident that the tetramethyl glucose did not originate in glucose or in cellobiose, but in a polyhexose containing more than two C_6 residues. If the methylated material which yielded the tetramethyl glucose consists of a single chemical individual,

it follows that ten C_6 groups are present, but, in such an event, the molecular weight would exceed 2000. If, on the other hand, the material is a mixture, one component must be a fully methylated reducing sugar containing any number of glucose residues from three to nine, the remaining constituent being the corresponding poly(trimethyl anhydroglucose). The number of possible mixtures which satisfy the analytical data is large and in the following table some typical examples are given, all of which possess practically the same composition and would give the results obtained in this investigation.

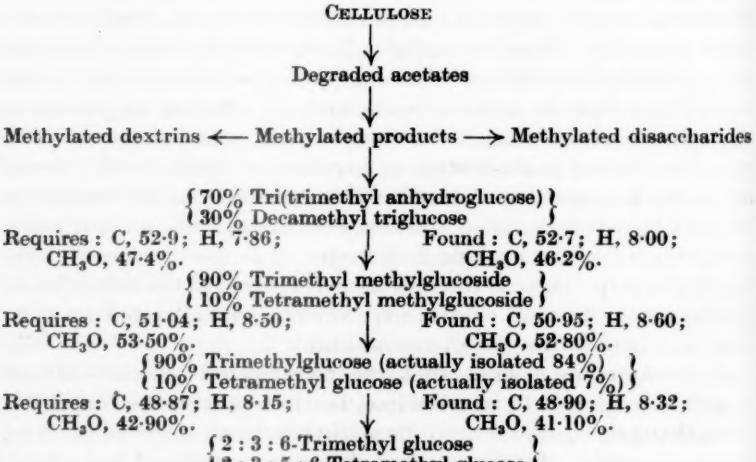
I. A mixture containing 70% of a tri(trimethyl anhydroglucose) and 30% of a methylated trisaccharide. (Molecular weight approximately 625.)

II. A mixture containing 60% of a tetra(trimethyl anhydroglucose) and 40% of a methylated tetrasaccharide. (Molecular weight approximately 834.)

III. A mixture containing 50% of a penta(trimethyl anhydroglucose) and 50% of a methylated pentasaccharide. (Molecular weight approximately 1043.)

IV. A mixture containing 40% of a hexa(trimethyl anhydroglucose) and 60% of a methylated hexasaccharide. (Molecular weight approximately 1251.)

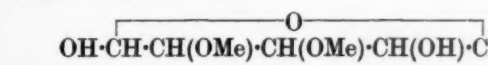
The list reveals that the molecular-weight determinations are discriminative and, as the value 656 was obtained, lead to a definite decision on the question of molecular magnitude. The consistency of our results is also displayed by the following scheme, which serves to simplify the series of reactions :


Cellulose
Degraded acetates
Methylated dextrins
Methylated products
Methylated disaccharides
70% Tri(trimethyl anhydroglucose)
30% Decamethyl triglucose
Requires : C, 52·9; H, 7·86; CH3O, 47·4%.
Found : C, 52·7; H, 8·00; CH3O, 46·2%.
90% Trimethyl methylglucoside
10% Tetramethyl methylglucoside
Requires : C, 51·04; H, 8·50; CH3O, 53·50%.
Found : C, 50·95; H, 8·60; CH3O, 52·80%.
90% Trimethylglucose (actually isolated 84%)
10% Tetramethyl glucose (actually isolated 7%)
Requires : C, 48·87; H, 8·15; CH3O, 42·90%.
Found : C, 48·90; H, 8·32; CH3O, 41·10%.
2 : 3 : 6-Trimethyl glucose
2 : 3 : 5 : 6-Tetramethyl glucose

Appendix.

Subsequent to the completion of the paper now communicated, the subject of the ring structure of glucose has been re-opened by Charlton, Haworth, and Peat (this vol., p. 89), who bring forward evidence that the stable form of the sugar is an amylene-oxide. That the oxydic ring in glucose may occupy different positions was first experimentally verified by one of us ten years ago, and the necessity to take all the different possibilities into account has repeatedly been emphasised (Irvine, "Some Constitutional Problems in Carbohydrate Chemistry," J., 1923, **123**, 900). For a considerable time it has been recognised by workers in this field that as the γ-oxydic formula for glucose depended on collateral rather than on direct experimental evidence, it might require modification and that to have the position of the oxygen ring settled experimentally would mark an advance in sugar chemistry. We do not commit ourselves at this stage to unqualified acceptance of the modified formula for glucose—the suggestion offered introduces a number of simplifications and is worthy of extended trial—but we defer our opinion until results obtained by the ultimate oxidation of tetramethyl glucose are available.

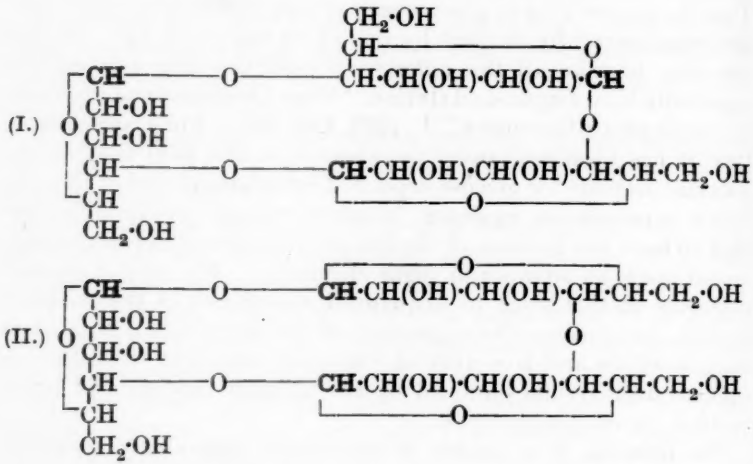
The formulæ of a number of methylated sugars may, however, be adjusted, *e.g.*, 2 : 3 : 5-trimethyl glucose would be described as the 2 : 3 : 4-form, but from the point of view of the present research greater importance is attached to the sugar known as 2 : 3 : 6-trimethyl glucose. A review of the constitutional study of this compound does not justify altering the position of the methyl groups, so that by shifting the ring to the neighbouring carbon atom the formula becomes :



The linkage present in cellulose would thus presumably be through positions 1 and 4 in place of 1 and 5 and the polysaccharide would therefore be described as poly-(1 : 4-anhydroglucose). It would, however, be premature to accept this conclusion as final, in view of the fact the particular variety of trimethyl glucose now under consideration can react as a γ-sugar. This possibility has been pointed out by Irvine and Hirst (J., 1922, **121**, 1221) in their study of the condensation of the compound with methyl alcohol, and it follows that the formation of this sugar is not absolutely diagnostic as to the structure of the complex from which it originates. This possibility and its effect on constitutional questions are discussed in a forthcoming paper.

The application of a poly(1 : 4-anhydroglucose) structure to

cellulose may now be considered and the opportunity may be taken to simplify the alternative structural formulæ applicable to this unit, as further consideration has shown that, provided α- and β-configuration is not taken into account, only two possibilities exist.* These as modified are :



The position of the potential reducing groups is indicated in block type.

In view of the results communicated in this paper, and taking into account the increasing importance attached to the formation of *iso*cellobiose from cellulose, it would be inadvisable to exclude formula II entirely. The retention of both types formulated above accounts for the formation of isomeric cellobioses and it is possible that both may function, although unequally, in the polymerisation process which leads to cellulose.

Experimental.

Graded Acetolysis of Cotton Cellulose.—The material employed was provided by Mr. William Rintoul of Messrs. Nobels, Ltd., and was identical with that used in our other investigations (see previous papers). Systematic experiments showed that when the temperature at which acetolysis is conducted is maintained uniformly at 15°, the best results were obtained when the reagent consisted of acetic anhydride and sulphuric acid in the ratio of 5·9 parts to 1 part

* I am indebted to Dr. A. Geake of the Shirley Institute (British Cotton Industry Research Association), who first kindly directed my attention to this simplification.—J. C. I.

by weight. These conditions having been established, the remaining factor, *viz.*, the duration of the reaction, was determined, in the first instance approximately, by microscopic examination of samples of the product. When precipitated by water, dissolved in alcohol, reprecipitated and dried, the material showed a wide range of solubility in organic solvents including benzene. These solutions, which were dextrorotatory, did not give films on evaporation and no trace of crystalline matter was visible in the residue, although control experiments with artificial mixtures showed that 3% of cellobiose octa-acetate can be detected in this way. Further, when dissolved in chloroform, the solution was practically optically clear when viewed in the ultramicroscope, a faint cone of light being, however, visible owing to the persistence of a small proportion of higher dextrins. The control experiments were conducted throughout the entire series of products ranging from a normal cellulose triacetate to cellobiose octa-acetate. A typical preparation is now described, but as the reaction is affected by numerous factors, including the surface condition of the cotton, it is necessary to state that in order to obtain consistent results the acetolysis must be standardised by the physical examination indicated above.

The cellulose (40 g.), dried at 110°, was added gradually to a mixture of 400 c.c. of acetic anhydride and 40 c.c. of sulphuric acid, the pasty mass being kept at 15° and thoroughly stirred for 5 hours. The cellulose was noticeably affected in 90 minutes and dissolved within 24 hours, giving a faintly yellow liquid. During the subsequent 72 hours the colour changed to orange, but the solution remained clear and as at this stage the ultramicroscopic test was satisfactory the liquid was poured into 4 litres of water. The solid thus precipitated showed a tendency to coagulate to a plastic mass which was disintegrated by grinding under water to give a fine flaky powder. After filtration, the product was thoroughly washed with water and dried slowly at 30—40°/10 mm. Thereafter it was dissolved in hot rectified spirit and reprecipitated by the addition of water. Average yield of dry solid = 50 g., when the duration of the acetolysis varied from 95 to 101 hours.

The material was only slightly soluble in hot absolute alcohol, but easily soluble in rectified spirit. It was also readily soluble in cold acetic acid, acetone or chloroform, but less so in benzene. It melted without decomposition, but the temperature of fusion varied between 120° and 160° in different preparations. Moisture (determined at 110°), 1·35%; ash, negligible; sulphur, absent. Found: C, 49·9; H, 5·8; Acetyl, 64·2. Cellulose triacetate requires C, 50·0; H, 5·55; Acetyl, 62·5%. The specific rotation varied

from about + 10° to + 20°, but in the work now described material was selected which gave the following values:

	Solvent.	c.	$[\alpha]_D$.
Preparation I.	Chloroform.	1·75	+20·3°
,, II.	,,	2·58	19·4
,, III.	Acetone.	1·76	22·1

The acetate reduced Fehling's solution and as this result is important experimental details are given. A weighed quantity (0·3289 g.) was dusted into an excess of boiling Fehling's solution, the boiling being continued for 4 minutes. The weight of dry cuprous oxide thus obtained was 0·1467 g. In order to determine the effect of hydrolysis on the reducing power, 0·3289 g. of the acetate was dissolved in 60% alcohol containing 6% of hydrogen chloride, and the solution was boiled under a condenser for 4 hours. Thereafter the alcohol was replaced by 8% aqueous hydrochloric acid, and the mixture again boiled for 8 hours. A trace of solid matter remained undissolved and the solution, which was practically colourless, was neutralised and added to boiling Fehling's solution. As the weight of cuprous oxide obtained was 0·3250 g., the ratio of the reducing power before and after hydrolysis is 1 : 2·2. Attempts to eliminate the reducing component of the mixture effected only negligible separation but revealed, as the following experiment shows, that little significance can be attached to melting points in these compounds.

18 G. of the acetate were dissolved in 250 c.c. of hot rectified spirit and, on cooling, a first fraction of 12 g. separated. On adding 270 c.c. of water to the mother-liquor a precipitate formed and after further dilution to 850 c.c. the liquid was set aside over-night. The second fraction thus obtained weighed 5·4 g.

	Original material.	Fraction I.	Fraction II.
M. p.	155°	130—140°	140—148°
C	49·9%	49·6%	49·6%
H	5·8%	5·75%	5·6%
$[\alpha]_D$ in chloroform	+18·5°	+20·3°	+19·4°

Molecular weight determinations by Rast's process or by the cryoscopic method in acetic acid gave very variable results, owing apparently to the presence of a small quantity of insoluble dextrin. The presence of this impurity was confirmed by digesting the acetate with 2*N*-sodium hydroxide at 25° for 3 hours. On neutralisation, a flocculent precipitate separated which darkened on washing and drying. This product, which was present only in small amount, had the properties of a dextrin, decomposed at 220°, and gave C, 44·5; H, 6·4% [$(C_6H_{10}O_5)_x$ requires C, 44·4; H, 6·2%].

Methylation of the Depolymerised Acetate.—As the direct replace-

ment of acetyl by methoxyl in one operation is not of general application, the details of a typical experiment are quoted. The acetate (46 g.) was suspended in 225 c.c. of 2*N*-sodium hydroxide and disintegrated by mechanical stirring. After the temperature had been raised to 30°, small equivalent quantities of methyl sulphate and 30% sodium hydroxide were added at short intervals and, when three-fourths of the reagents had been introduced, the temperature was gradually raised to 70° and maintained at this point until the remainder of the methylating mixture had been added. Total reagents used : 110 c.c. of methyl sulphate and 110 g. of sodium hydroxide in 180 c.c. of water.

After completion of the reaction by heating at 100° for 35 minutes, the product remained in solution and was extracted with chloroform. The extract was dried and the solvent removed, when a clear syrup remained which set on cooling to a glass. Yield, 14 g.; OMe, 38·1%. The products of three similar preparations were united and subjected to three further methylations. As the methoxyl content increased, the solubility in alkali diminished so that the methylated product could be removed by filtration and, an important point, the process of chloroform extraction was discontinued so that the disaccharide derivatives remained in the alkaline liquor. Yield, 30 g.; OMe, 45·6%. Five subsequent methylations did not affect the methoxyl content, which agrees exactly with that required for a trimethyl cellulose.

The product was ground to a white solid and extracted repeatedly with boiling ether, which left a small residue (6%) undissolved. This had OMe, 43·7%, and was evidently derived from the cellulose dextrin present in the starting material. On removal of the solvent ether, the main product (94%) was isolated as a clear, colourless glass which could be powdered to a fine white solid softening at about 40°. This proved to be essentially tri(trimethyl 1 : 5-anhydroglucose) mixed with the corresponding methylated trisaccharide. Properties : readily soluble in cold ether, chloroform, benzene, or acetone, less soluble in methyl alcohol, rectified spirit or water; no action on Fehling's solution until after acid hydrolysis. Found : C, 52·7; H, 8·0; OMe, 46·2. A mixture of 70% of tri(trimethyl anhydroglucose) and 30% of a fully methylated trisaccharide requires C, 52·9; H, 7·9; OMe, 47·4%.

Solvent.	*c.*	$[\alpha]_D$.
Chloroform	3·564	+7·0°
Benzene	1·682	10·1
Acetone	3·367	15·7

Molecular Weight.—The mean of two determinations by Rast's method was 662. The mean of three consistent results by the

cryoscopic method with benzene as solvent was 663, and an independent repetition of the same process gave 642. The calculated value for the mixture postulated above is 625.

Simultaneous Hydrolysis and Condensation with Methyl Alcohol.—The mixture of methylated trisaccharide derivatives (4·3552 g.) was dissolved in methyl alcohol containing 1% of hydrogen chloride and heated at 110° for 70 hours. The solution, which was pale yellow and contained no suspended matter, was then neutralised with silver carbonate, filtered, and evaporated to dryness. 4·562 G. of a colourless glucosidic syrup remained, corresponding with a yield of 92% of the theoretical maximum. On distillation, the liquid boiled at 115°/0·3 mm. and 3·87 g. were collected in two fractions to permit of duplicate analyses. On the basis that the original methylated is a mixture of 70% of tri(trimethyl anhydroglucose) and 30% of a fully methylated trisaccharide, the above product of hydrolysis should consist of trimethyl methylglucoside (90%) and tetramethyl methylglucoside (10%). This was verified by analysis. Fraction I: C, 50·9; H, 8·3; OMe, 52·6. Fraction II: C, 50·95; H, 8·6; OMe, 52·8%. Calculated for the mixed glucosides: C, 51·0; H, 8·5; OMe, 53·5%.

Hydrolysis of the Mixed Glucosides.—The syrup (2·67 g.) was dissolved in 110 c.c. of 8% hydrochloric acid, a trace of charcoal added, and the solution boiled under a condenser until the rotation was constant. The subsequent treatment was as usual and as the mixed sugars, isolated initially as a syrup, weighed 2·2 g., the yield was 88%. In order to separate the sugars, the syrup was dissolved in water, and the solution thoroughly extracted with chloroform. The aqueous solution was evaporated to dryness under diminished pressure, the resulting syrup being redissolved in absolute alcohol which was, in turn, evaporated. Finally, the sugar was dissolved in pure dry ether and after filtration the solvent was slowly evaporated. On nucleation with 2 : 3 : 6-trimethyl glucose, the product solidified to a hard mass of crystals (1·85 g.), m. p. 105°; permanent $[\alpha]_D$ in water, for $c = 1{\cdot}058$, + 71·8° (Found: C, 48·5; H, 8·05; OMe, 41·6. Calc.: C, 48·65; H, 8·1; OMe, 41·9%).

The remaining methylated sugar was isolated from the chloroform solution, which was dried and evaporated, as a syrup weighing 0·25 g. This crystallised on keeping and, when purified from light petroleum, gave pure 2 : 3 : 5 : 6-tetramethyl glucose displaying the standard physical constants. Yield of trimethyl glucose : yield of tetramethyl glucose = 84% : 7%. Calc., 90% : 10%.

Direct Hydrolysis of the Methylated Product.—A 5% solution in 8% hydrochloric acid was fully hydrolysed on boiling for 30 minutes, and the sugars formed were isolated by standard methods. The

product was a clear syrup which, in accordance with the composition of the starting material, should consist of trimethyl glucose (90%) and tetramethyl glucose (10%) (Found: C, 48·9; H, 8·3; OMe, 41·1. The above mixture requires C, 48·9; H, 8·15; OMe, 42·9%).

Deacetylation of the Degraded Cellulose Acetates.—20 G. of the finely-powdered acetate were added to 66 c.c. of 33% aqueous dimethylamine. An appreciable rise of temperature took place and the liquid was cooled to 15° and kept, with frequent shaking, for several days. For the first 48 hours the liquid thickened, but after 96 hours it had become much more mobile. After 9 days, water was added and insoluble dextrins were removed by filtration through charcoal, the filtrate being evaporated to dryness under diminished pressure. A golden syrup remained which was thoroughly mixed with successive quantities of ether to remove acetodimethylamide, the undissolved residue being dissolved in a little water and precipitated by excess of absolute alcohol. A white, amorphous powder was thus obtained (1·85 g.) which sintered at 170° and melted with decomposition at 180° (Found in material dried in a vacuum at 110° until of constant weight: C, 42·3; H, 6·6; *M*, cryoscopic in water, 315. A disaccharide requires C, 42·1; H, 6·4%; *M*, 342). The product is therefore a disaccharide other than cellobiose; it reduced Fehling's solution both before and more particularly after hydrolysis with acids. For $c = 4{\cdot}2735$, $[\alpha]_D^{20°}$ was $+ 14{\cdot}04°$, no mutarotation being observed within 24 hours.

The alcohol mother-liquor which had yielded the above disaccharide gave on evaporation under reduced pressure 6·4 g. of a syrup. This was dissolved in water, the solution agitated with chloroform to remove traces of acetodimethylamide, and the aqueous portion neutralised and recovered. By means of fractional extraction with boiling alcohol, the material was separated into two portions, but it was found impossible to eliminate dimethylaminoglucosides, and consequently this section of the investigation is being continued by different methods.

Acknowledgment is made to the Carnegie Trust for the award of a Fellowship which enabled one of us to take part in the investigation.

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CXCV.—*The Constitution of Polysaccharides. Part X. The Molecular Unit of Starch.*

By James Colquhoun Irvine and John Macdonald.

We have naturally included the important case of starch as part of our programme of research on the constitution of polysaccharides, applying the same principles and methods as in the analogous examples of cellulose and inulin. The same limitations have also been imposed on the scope of the investigation, which has been confined meanwhile to determining the linkage of the individual glucose residues in starch so as to arrive at the structure of the simplest molecule (or molecules) which, by polymerisation, form the polysaccharide. Our work has not been concerned with the magnitude of these polymerides or with the individual constituents of starch, nor has it included the differences between one variety of starch and another so far as these may be attributed to variations in the nature and amount of extraneous compounds rather than to inherent differences in molecular structure.

Hitherto, the experimental evidence applicable to the constitutional study of starch has been obtained mainly through biochemical agency and, in introduction to the present communication, only two types of such reactions may be selected from the abundant literature on this subject. These are : (*a*) the conversion of starch into a series of simple amyloses in each of which the empirical formula $(C_6H_{10}O_5)_n$ is retained, and (*b*) the formation, through changes which are in part hydrolytic, of maltose, *iso*maltose, and, ultimately, of glucose. An adequate structural representation of starch must accommodate the above reactions and it is evident that the constitution of maltose is of special importance as bridging the gap between the closed-ring structure of the polyamyloses and the C_6-chain of glucose. Generally speaking, the application of ordinary chemical methods has led to few results which bear directly on the constitution of starch, as the processes of substitution and disruption are not sharply differentiated. An exception is provided, however, in the method of methylation, by means of which the hydroxyl groups in starch may be substituted by methoxyl groups which survive hydrolysis, thereby giving a methylated glucose. Work on these lines was commenced in this laboratory 6 years ago, but no detailed account of our results has so far been published, although reference has been made occasionally to some of the conclusions at which we have arrived. The delay has been due, not so much to the fact that the methylation of starch presented severe

experimental difficulties, as to the necessity which arose to suspend the research and devote a series of separate investigations to the constitution of maltose. Meanwhile, other workers have attempted to convert starch into its fully methylated derivative, but have failed, it having been found impossible to replace all the hydroxyl groups by methoxyl. Our experience in this respect was, at first, no different, and consequently we were compelled to subject an incompletely methylated starch to hydrolysis and to separate the mixture of methylated glucoses thus produced. In such constitutional studies, this is unsatisfactory procedure and cannot be regarded as giving an adequate view of structure, but our earlier work revealed that an invariable product of the reaction was a crystalline sugar, which was identified as 2 : 3 : 6-trimethyl glucose. This result was altogether unexpected. Unless the action of diastase on starch is in part synthetic, there can be little reason to doubt that, in the starch molecule, glucose residues are joined in the same manner as in maltose, and it follows that the trimethyl glucose obtainable from starch should be identical with that from maltose. Haworth and Leitch, however, state that the disaccharide gives 2 : 3 : 4-trimethyl glucose, and the formula for maltose advocated by these authors, either in its original form (J., 1919, **115**, 809) or as subsequently modified (Charlton, Haworth, and Peat, this vol., p. 99), does not admit of the formation of 2 : 3 : 6-trimethyl glucose from any compound containing the maltose structure. The evidence before us was thus conflicting. Obvious sources of error, such as the possible presence of hemi-celluloses, had been carefully excluded, but other explanations suggested themselves, one being that the glucose residues in starch might not be symmetrically attached to each other, as one pair might possess the maltose structure and another the linkage characteristic of cellobiose. This idea was expressed in formulæ (*Brit. Assoc. Reports*, 1922, 33; J., 1923, **123**, 898) in which an attempt was made to reconcile our results with those from which the structure of maltose was deduced, but further investigation showed that no satisfactory formula for starch could be constructed on the basis of Haworth's constitution of maltose. This became apparent when we succeeded in methylating starch completely, as, on hydrolysing the product, 2 : 3 : 6-trimethyl glucose was obtained in yields which showed that this sugar must be regarded as the essential and not as an adventitious product of the series of reactions. Concurrently, and by arrangement with Professor Pringsheim, hexa-amylose was subjected similarly to methylation and hydrolysis. The result was equally emphatic, as the same crystalline sugar was obtained as from starch. Finally,

the tri-hexosan prepared by the depolymerisation of starch (Pictet, *Helv. Chim. Acta*, 1922, **5**, 640; 1924, **7**, 932) was similarly treated and was likewise found to give the same variety of trimethyl glucose.

Only two alternative conclusions could be drawn from the above discordant evidence; the first, that maltose has no structural relationship to starch, was rejected as improbable and we were forced to the opinion that the constitution attributed to maltose was incorrect. This we have ascertained to be the case (Irvine and Black, this vol. p. 862), it having been shown that, in common with starch, polyamyloses and cellulose, maltose yields 2 : 3 : 6-trimethyl glucose unmixed with the 2 : 3 : 4-isomeride. The present communication is therefore submitted on the basis of a corrected constitution for maltose.

We find that the methylation of starch displays a number of features which distinguish the polysaccharide from either cellulose or inulin. Methyl groups are introduced fairly readily by repeated action of methyl sulphate and alkali, but the methoxyl content quickly reaches a limit of 36—37%, this value indicating that only seven hydroxyl groups out of nine have undergone alkylation. Methylated starch of this composition appears to be a definite compound possessing a characteristic optical activity, and, in consequence, the conclusion might be drawn that there are not three hydroxyl groups in each C_6 unit. This inference would be unwarranted, however, as the partly methylated starch was capable of acetylation to the exact extent required to substitute the remaining hydroxyl positions. Further, the methylated starch, when regenerated from the acetate, still preserved its resistance to further methylation. Another distinguishing property displayed by starch during methylation is that the reaction is definitely arrested at the dimethyl stage when conducted by means of silver oxide and methyl iodide. When these reagents are applied to a methylated starch containing less than two methoxyl groups per C_6 unit, the methoxyl content is increased to 32—33%, but no further. Similarly, the same reagents have only a limited effect in raising the methoxyl content when applied to methylated starch which has been alkylated by means of methyl sulphate beyond the dimethyl stage. In the above respects, starch resembles the polyamyloses closely and presents features which are also recognisable in the case of maltose. As the methylation of starch proceeded, the colour reaction with iodine vanished, the usual progressive changes in solubility were observed, and the rotation increased in the dextro-sense. Simultaneously, the protein and inorganic constituents were eliminated, particularly when the

silver oxide reaction was employed, as, in this case, they were precipitated in the form of insoluble double compounds with silver iodide. It is important to observe that these precipitates contained combined carbohydrate, thus indicating that nitrogen and phosphorus form part of the polymerised aggregate. In consequence, the same methylated starch was finally obtained, irrespective of the starting material used, but in large-scale experiments we employed only purified rice-starch. Reference to the experimental details will indicate the manner in which the derivatives of hemi-celluloses were removed so as to separate constituents which would otherwise have introduced complications.

Although four successive applications of methyl sulphate and alkali converted the polysaccharide into a derivative containing 37% of methoxyl, this did not represent the limit of the reaction. Subsequent methylations slowly increased the methoxyl content and, after 24 treatments, the value (43·7%) agreed closely with that required for a trimethyl starch. There are thus three distinct stages observable in the alkylation, the products in each case displaying a constancy in composition and properties which warrants the conclusion that they are three consecutive compounds. These are :

		% OMe (found).	Ratio of OMe groups to initial OH groups.	$[\alpha]_D$ in $CHCl_3$.
I.	Dimethyl starch	32·7	6 : 9	+135·7°
II.	Methylated starch	36·3	7 : 9	169·5
III.	Trimethyl starch	43·7	9 : 9	216·5

It will be observed that the specific rotation increased regularly with the rise in methoxyl content, and this behaviour we have verified over a wide range in composition, thus affording powerful evidence that frequent repetition of the methylation process does not cause structural rearrangement.

The hydrolysis of each type of methylated starch was undertaken, the method of heating with methyl alcohol and hydrogen chloride being employed so as to isolate the liberated sugars in the form of the corresponding methylglucosides. Compound I gave essentially a dimethyl methylglucoside, the description of which is deferred to a later communication, while II yielded a mixture from which 2 : 3 : 6-trimethyl methylglucoside (1 mol.) was isolated, together with a dimethyl methylglucoside (2 mols.). In the case of III (trimethyl starch) the reaction furnished a conclusive result, as 2 : 3 : 6-trimethyl methylglucoside melting at 57·5° was obtained in excellent yield. A careful search for the isomeric 2 : 3 : 4-form was made, both by fractional distillation and by fractional crystal-

lisation of the glucoside, but no trace of this compound was detected. These results were confirmed by hydrolysis of the total glucosides with aqueous acid and isolation of crystalline 2 : 3 : 6-trimethyl glucose. All syrupy products were examined, but the 2 : 3 : 4-isomeride was definitely absent.

In the course of this section of our work it was necessary to compare critically the constants of the isomeric 2 : 3 : 6- and 2 : 3 : 4-trimethyl β-methylglucosides, as these compounds, which show a close resemblance, have been utilised in certain structural studies of disaccharides as a means of discriminating between the isomeric trimethyl glucoses. The following values were determined on specimens of the compounds obtained either by the limited action of methyl alcohol and hydrogen chloride or through the agency of the corresponding acetobromo-derivatives.

	Source.	M. p.	$[\alpha]_D$.
2 : 3 : 6-Trimethyl methyl-glucoside.	2 : 3 : 6-Trimethyl glucose from cellulose, or Trimethyl starch.	57·5°	−29·3° in MeOH
2 : 3 : 4-Trimethyl methyl-glucoside.	2 : 3 : 4-Trimethyl glucose (synthetic), or Trimethyl glucosan.	93—94	−23·1 in MeOH

The glucosides cannot be distinguished with certainty through their specific rotations, and the melting points, although far apart, are greatly affected by impurities or by the presence of varying proportions of α- and β-forms. It follows that trustworthy identification of these reference compounds is possible only when both the melting point and the specific rotation agree with the standard values. In addition, the polarimetric curve of the hydrolysis of each compound is diagnostic, and in the case of the equilibrium mixture of the α- and β-2 : 3 : 6-isomerides displays two maxima separated by a minimum. The identification of these isomeric glucosides is nevertheless difficult and failure to discriminate between them may lead to erroneous conclusions as to structure. In this connexion, it may be recalled that Haworth and Wylam (J., 1923, **123**, 3125) obtained from gentiobiose a trimethyl methylglucoside melting at 92·5° and showing $[\alpha]_D$ −25·1° in methyl alcohol. This was regarded as the 2 : 3 : 4-variety, a conclusion which is doubtless correct. But in studying the constitution of raffinose (Haworth, Hirst, and Ruell, J., 1923, **123**, 3131) another preparation, possessing nearly the same specific rotation, but melting at 74°, is also claimed to be 2 : 3 : 4-trimethyl methylglucoside. The statements are irreconcilable, as, if the melting point of the latter preparation was depressed by the presence of the stereoisomeric α-form, the specific rotation would

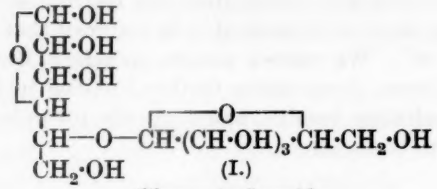
not remain the same, but would be displaced in the dextro-direction. In our examination of these glucosides we have never encountered a form of 2 : 3 : 4-trimethyl methylglucoside melting at 74° and the inconsistency becomes more acute if it be assumed that this figure is a misprint for 94°. We cannot accept, therefore, Haworth's constitution for raffinose, a conclusion further justified by the fact that it contains a melibiose residue based on the formula for maltose recently shown to be incorrect.

Discussion of Results.

As starch is not a uniform homogeneous polysaccharide, limitations must be placed on any discussion regarding constitution, but the results now contributed afford proof that starch consists essentially of a mixture of polymerides which are based on the same molecular unit. The structural similarity displayed by these constituents lies in the fact that there are three hydroxyl groups present in the same positions in each C_6 chain, and it is thus possible to elucidate the constitutional factors which are common to all the components. The expression " starch," as used in this discussion, applies therefore to constituents, amounting to 60—70% of the total, which conform to the above generalisation in that they are convertible into 2 : 3 : 6-trimethyl glucose, but differ in the degree of polymerisation.

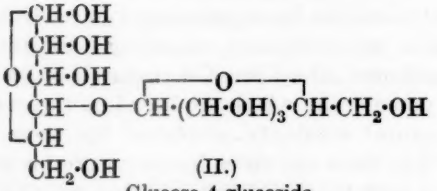
The possibility that starch may be derived from β-glucosan has already been rejected and is again refuted by the results of the present investigation. There remains consideration of the relationship to maltose and to *iso*maltose, but here complications are at once encountered. These difficulties are due in part to inadequate knowledge of *iso*maltose, but are mainly attributable to the confusion which has arisen regarding the constitution of the diglucoses as a class. So far, three disaccharides (maltose, cellobiose, and *iso*cellobiose) have been shown to be convertible into 2 : 3 : 6-trimethyl glucose, and the present research clearly points to the idea that *iso*maltose will be found to give precisely the same result. The formation of the above trimethyl glucose cannot, in consequence, be regarded as final evidence of the linkage of two glucose residues, as such a result fails to discriminate between two alternatives. It follows, also, that the oxydic ring in glucose cannot be restricted to the amylene-oxide linkage alone, as otherwise it would be impossible to formulate all the diglucoses in terms of their properties. For example, the disaccharides postulated below are definitely isomeric and contain glucose residues with different oxygen rings, but each compound would be convertible into 2 : 3 : 6-trimethyl glucose, type I giving in the first place the γ-form of the sugar which

reverts to the stable variety, while type II would give the same final product directly.



(I.)

Glucose 5-glucoside.

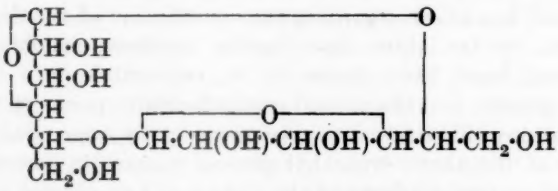


(II.)

Glucose 4-glucoside.

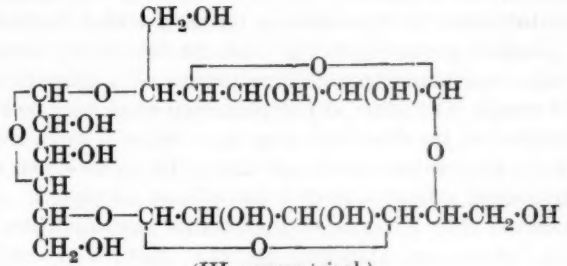
It may be presumed that as cellobiose and *iso*cellobiose form one structural pair, maltose and *iso*maltose will form the other, and the above types can therefore accommodate all four sugars. Pending the completion of further experimental work now in progress, it is inadvisable definitely to assign maltose and cellobiose to their respective types, but, in order to render the present discussion intelligible, formula I may be ascribed arbitrarily to maltose, in which case cellobiose conforms to formula II.

If starch is based on an anhydro-disaccharide unit, the simplest formula for the unpolymerised molecule becomes :

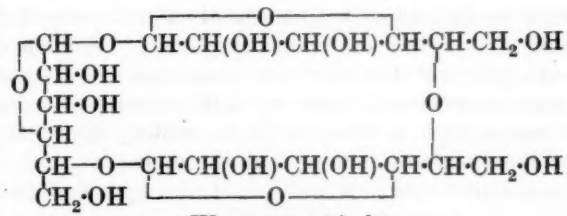


The hydrolysis of the " maltosan " postulated above would give maltose as the only disaccharide, the change including opening of one anhydro-linking followed by adjustment of the unstable oxygen ring in the non-reducing glucose component. Taking into account the difficulty in certifying that any preparation of maltose consists of a single homogeneous chemical individual, it is doubtful if the yield of maltose from starch is as great as that which would be given by a compound of the maltosan type. It would not be justifiable, however, at this stage to exclude maltosan as one of the molecular

units of starch, particularly as polyamyloses exist which contain an even number of C_6 chains. The formula does not, however, admit of the formation, from starch, of a trihexosan or tri-amylose, and consequently consideration must also be given to a constitution based on the union of three glucose residues. Two possibilities exist :



(III, symmetrical.)



(IV, unsymmetrical.)

No conclusive evidence exists which would serve to discriminate between these possibilities. A compound possessing formula (III) could undergo hydrolysis to give only maltose and glucose, whilst, according to formula (IV), maltose, an *iso*maltose and a non-reducing diglucose might result. This is perhaps improbable, as the existence of such hydrolysis products could scarcely have escaped detection, but, in any case, neither of the formulæ reveals the α- or β-configuration of the individual glucose residues. The structures thus fail to account for the fact that starch is convertible into maltose under one set of conditions and into *iso*maltose when the conditions are changed. Similarly, they do not explain why the polyamyloses can be classified in α- and β-series.

We do not share the view that the α- or β-configurations of the methylated glucosides obtained from trimethyl starch afford a true index of the glucose configuration in the starch molecule and purely chemical methods of investigation throw little light on this important aspect of the structural problem. This evidence is, however, rapidly being accumulated in the important researches of Ling and Nanji, and if the results obtained by these workers are not utilised in the

present discussion it is owing solely to the desire to avoid trespass on their field of work.

Limiting the discussion to conclusions drawn from chemical reactions alone, the structures elucidated above may now be tested according to the peculiar behaviour of starch during methylation. The formation of a definite dimethyl starch (*i.e.*, 6 hydroxyl groups out of 9 substituted) is explained in terms of either formula, as the primary alcohol groups are the last to be methylated. Both formulæ also accommodate the production of a trimethyl starch but only formula (IV) offers any explanation as to why methylation can be arrested at the dimethyl stage (*i.e.*, when 6 hydroxyl groups out of 9 have been substituted) and thereafter slows down abruptly when 7 hydroxyl groups out of 9 have been alkylated. For this reason, formula (IV) is retained for further consideration. Much importance must be attached to the fact that methylated starch containing 37% of methoxyl is a definite compound which breaks down on hydrolysis to give exactly 2 molecules of dimethyl glucose and 1 molecule of trimethyl glucose. Reference to the experimental part will show that this compound was obtained under varying experimental conditions on eight successive occasions, so that the composition ascribed to it is unlikely to be fortuitous. Accepting this result, it follows that the molecular unit of starch must contain either nine or a multiple of nine hydroxyl groups. In other words, the simplest unit would be a trihexosan and the next possibility a hexahexosan. In order to explain the existence of polyamyloses containing an even number of C_6 chains, it is, however, necessary to select the hexahexosan as the basal unit, so that the cyclic formulæ given above must be doubled, with a corresponding increase in the structural possibilities involved.

It is thus apparent that, approaching the study of starch by strictly chemical methods, conclusions are reached in close agreement with those arrived at in recent studies of enzyme action. It will be equally apparent that both types of investigation are necessary to solve the main factors involved in the starch problem, (1) the α- or β-configuration of adjacent hexose residues, (2) the positions through which these residues are coupled, and (3) the degree of polymerisation undergone by the basal unit.

The research, which we regard only as preliminary, is being continued in various directions.

Experimental.

The starting material used in the research consisted of purified wheaten, potato, or rice starch, but the first-mentioned variety was discarded in favour of the others, which were found to give the same

methylated derivatives. To facilitate description, it may be stated that, throughout the work, all evaporations and distillations were conducted under reduced pressure.

Dimethyl Starch.—With a few modifications, the methylation was carried out as described by Irvine and Steele (J., 1920, **117**, 1474) in the parallel case of inulin, and the following is the account of one typical experiment. 32 G. of starch were mixed with 150 c.c. of water and stirred mechanically whilst 160 c.c. of 12½% sodium hydroxide solution were added. This had to be conducted slowly, as otherwise the starch coagulated to a stiff jelly, a condition which is unsuitable for methylation. Thereafter, 140 c.c. of 50% sodium hydroxide solution and 80 c.c. of methyl sulphate were run in simultaneously, the addition being extended over 3 hours and adjusted so as to maintain the alkaline reaction. The liquid was kept at 35° and was vigorously stirred during the reaction, which was completed by heating at 100° for 40 minutes. After cooling, an equal volume of rectified spirit was added, and carbon dioxide passed through the solution for a prolonged period. The precipitated sodium salts were then removed by filtration through linen, and the filtrate was cautiously neutralised with dilute sulphuric acid. If kept over-night, a crop of sodium sulphate and sodium methyl sulphate separated, but as part of the product was retained by the crystals it was advisable to evaporate the liquid to a thick syrup and repeat the methylation a second time on the total product. In this and similar evaporations it was necessary to add barium carbonate, as otherwise acidity developed and hydrolysis occurred. For the same reason, the temperature was restricted to under 60°.

The aqueous-alcoholic solution of the product, obtained after the second methylation, was evaporated to dryness, and the residue extracted repeatedly with a large excess of boiling chloroform. The inorganic residues were similarly treated and yielded a further quantity of the methylated product showing the same composition (OMe, 22·7—23·6%). A third methylation was conducted on the material extracted by chloroform and thereafter the methylated starch was completely soluble in aqueous alcohol and was no longer occluded by the inorganic salts. The isolation of the product by extraction with chloroform was carried out as already described, but difficulty was experienced in filtering the chloroform solution by ordinary methods, as the methylated starch formed continuous films on the filter-paper. On removal of the solvent, a stiff syrup remained, readily convertible into a white powder; soluble in cold water, hot alcohol, and in chloroform, insoluble in ether. Traces of reducing sugars were present and the aqueous solution gave a

yellow colour with iodine which was not discharged on heating. OMe = 27·2%. Yield 22 g.

The silver oxide reaction was now applied to the product, which was boiled with excess of methyl iodide to which methyl alcohol was gradually added until the solution became comparatively clear. Silver oxide (51 g.) was then added in small amounts, and the mixture kept at the boiling point for 8 hours. Boiling ethyl alcohol was used as the extracting agent, the turbid solution being evaporated and the residue dissolved in chloroform. The silver salts were also extracted in a Soxhlet apparatus with the same solvent, the extracts being united and the product recovered. Repetition of the alkylation in the same manner had very little effect on the methoxyl content, but, apparently owing to depolymerisation, the solubility of the product in methyl iodide increased steadily with each treatment. Concurrently, and contrary to general experience, the experimental loss increased with the solubility in methyl iodide.

No. of silver oxide methylations.	Wt. of methylated starch.	Vol. of MeOH required.	Methoxyl content.
1	21 g.	65 c.c.	27·8%
2	19	39	28·8
3	15	20	28·6
7	6	3	28·9

The loss in yield was due to combination of part of the product with silver iodide as in the case of methylating glucosamine (Irvine and Hynd, J., 1912, **101**, 1128). On extracting the plastic solid with boiling water for several hours the solution contained carbohydrate, a secondary amine and phosphate.

Various attempts to purify the methylated starch obtained by the above operations were made, the most successful being boiling in chloroform solution with charcoal, but as this involved loss the material was separated into two portions by allowing an ethyl alcohol solution to stand in the cold. Any insoluble syrup which separated was removed and again methylated by the silver oxide reaction, so that ultimately the entire product was obtained in the soluble form. As the material had now acquired complete solubility in methyl iodide, two further methylations were given without the use of any extraneous solvent. In this way, dimethyl starch was obtained as a white powder, free from mineral matter and soluble in water, the solution giving no colour with iodine (Found : C, 50·4; H, 7·4; OMe, 32·7. Dimethyl starch requires C, 50·5; H, 7·4; OMe, 32·7%). $[\alpha]_D$ in chloroform + 135·7° for $c = 1·916$.

Hydrolysis of Dimethyl Starch.—This reaction was conducted in the first place by heating a dilute solution in 2·5% hydrochloric acid on a boiling water-bath for 3 hours. As the solution remained turbid,

the acid concentration was raised to 4% and heating was continued for an additional 3 hours, the reaction being completed by raising the temperature to 110° for 30 minutes. On filtering, a small quantity of a brown solid remained behind, and as this material still contained methoxyl it apparently consisted of one component of dimethyl starch which is highly resistant to hydrolysis. The clear filtrate, containing dimethyl glucose in solution, was treated so as to remove organic acids and was finally extracted with boiling acetone. The extract contained a thick syrup which when dissolved in ethyl acetate partially crystallised, but the solid could not be isolated in sufficient amount for identification. The solubilities, rotation and analytical composition of the syrup were, however, identical with those ascribed to 2 : 3-dimethyl glucose (Irvine and Scott, J., 1913, **103**, 575). Yield 75%. $[\alpha]_D$ + 50·3° in acetone for $c = 1$ (compare 2 : 3-dimethyl glucose, $[\alpha]_D$ + 50·9° in the same solvent).

Preparation of Methylated Starch.

The expression " methylated starch " is applied to the derivative in which seven hydroxyl groups out of nine have undergone methylation, the formation of this compound being characterised by a sharp cessation in the methoxyl increase. In each experiment, 32 g. of starch were used, the initial procedure being as described in the preparation of the dimethyl derivative. After four successive treatments with methyl sulphate, the insolubility of the product in the alkaline liquor enabled the isolation to be greatly simplified. The liquid was poured away from the coagulated mass of organic material and the latter was dissolved in boiling rectified spirit, the solution being neutralised with dilute sulphuric acid. After removal of the precipitated sodium salts, the filtrate was evaporated in the presence of barium carbonate, and the residue extracted with boiling chloroform. Removal of the solvent left a stiff syrup which was boiled with dry ether to remove traces of solvent, a treatment which converted the product into a white flaky powder (Found in material dried at 100°/15 mm.: C, 51·1; H, 7·6; OMe, 35·5. " Methylated starch " requires C, 51·2; H, 7·5; OMe, 37·0%). Yield 21 g.

When the above methoxyl content had been attained the application of the silver oxide reaction had practically no effect on the composition (Found: C, 51·1; H, 7·5; OMe, 36·3%; $[\alpha]_D$ in methyl alcohol + 186·3° for $c = 1·934$, in chloroform + 168·1° for $c = 2·029$). Methylated starch displayed the same range of solubility as dimethyl starch and similarly had no action upon Fehling's solution. When acetylated by means of acetic anhydride in presence of sodium acetate, it was converted into a granular acetate showing $[\alpha]_D$ in chloroform + 191·7°. The acetyl content (11·8%) agreed

with the value calculated on the basis that two out of nine hydroxyl groups originally present in starch resisted methylation and, on subjecting the acetate directly to the methyl sulphate reaction, the original material was regenerated (OMe = 36%).

Similarly, the use of diazomethane was ineffective in raising the methoxyl value, which remained remarkably steady in eight successive preparations of methylated starch (Found : OMe, 35·6; 35·4; 35·2; 36·3; 35·8; 35·2; 35·4; 35·5%). The specific rotation in chloroform also showed little variation, the extremes being $[\alpha]_D$ + 151·5° and 152·6° for $c = 1·25$. These results point to the idea that methylated starch is a homogeneous definite compound, but it may be emphasised that the above specific rotation is greatly increased if in the preparation of the compound the methyl sulphate reaction is supplemented by treatment with silver oxide and methyl iodide. Typical examples are quoted :

Methylations.				
(*a*) With methyl sulphate.		(*b*) With methyl iodide.	$[\alpha]_D$.	Solvent.
4	followed by	1	+168·1°	Chloroform.
4	,,	3	169·5	,,
5	,,	2	173·9	,,
4	,,	3	186·2	Methyl alcohol.

Reasons exist for the belief that this alteration in rotatory power is attributable to depolymerisation.

Hydrolysis of Methylated Starch.

A 10% solution of methylated starch in methyl alcohol containing 1% of hydrogen chloride was kept at the boiling point until the activity was nearly constant. Initially, the solution was opalescent, but rapidly cleared so that accurate readings were possible. Some typical results are quoted below, the complete series giving a smooth, unbroken curve.

Time from start (hours) ...	2	3	5	6	7	8
$[\alpha]_D$	+114·4°	+99·8°	+81·7°	+75·0°	+70·3°	+69·8°

The product, consisting of a mixture of methylated glucosides, was isolated in the usual manner and formed a clear viscous syrup. Practically the whole of the material dissolved in boiling ether and the syrup obtained on removal of the solvent was dried at 100°/1 mm. Yield 21·8 g. from 23 g. of methylated starch.

The two components, *viz.*, trimethyl and dimethyl methylglucosides, were separated by a tedious method which need not be described as it has been superseded by a superior process. The trimethyl methylglucoside was finally distilled at 120°/0·7 mm. as a colourless liquid (n_D 1·4585) which crystallised. When purified

from light petroleum, the crystals melted at 57° and showed $[\alpha]_D$ −20° in methyl alcohol (Found: C, 50·6; H, 8·5; OMe, 52·2. Calc. for trimethyl methylglucoside: C, 50·8; H, 8·5; OMe, 52·5%). The glucoside was converted into crystalline tetramethyl glucose by the usual processes, thus showing that it belongs to the stable type, and when hydrolysed with aqueous hydrochloric acid gave crystalline 2 : 3 : 6-trimethyl glucose in 94% yield (mutarotation in methyl alcohol + 83° ⟶ 68·3°. OMe, 41·8. Calc. for trimethyl glucose, 41·9%). A careful search for tetramethyl glucose and for 2 : 3 : 4-trimethyl glucose gave entirely negative results. The dimethyl methylglucoside fraction distilled at 140°/0·4 mm. as a viscous liquid (Found: C, 48·6; H, 8·1; OMe, 42·0. Calc.: C, 48·6; H, 8·1; OMe, 41·9%). As the compound was unknown, it was examined in some detail. On complete methylation, it was converted into tetramethyl methylglucoside, the β-isomeride being present in excess, and when condensed with benzaldehyde it gave a benzylidene derivative. This crystallised imperfectly and could not be characterised definitely as the benzylidene dimethyl methylglucoside described by Irvine and Scott (J., 1913, **103**, 575), although the similarity was very marked. Hydrolysis of the glucoside with aqueous hydrochloric acid gave the corresponding dimethyl glucose as a clear glass. This had the correct analytical composition and showed $[\alpha]_D$ + 56·6° in acetone solution, but the material failed to crystallise. The sugar formed no phenylosazone and did not condense with acid acetone, properties which further suggest that the compound was 2 : 3-dimethyl glucose, but oxidation with nitric acid under the conditions described by Haworth and Leitch (*loc. cit.*) gave a complex mixture. It was, in fact, the study of this reaction which directed our attention to the untrustworthy nature of such oxidations.

With regard to the yields of the glucosides obtained from methylated starch it is important to note that tetramethyl methylglucoside was absent and monomethyl methylglucoside was present to an extent not exceeding 5%. The ratio of the dimethyl to the trimethyl methylglucoside was 1·85 : 1, a result which shows that 2 molecules of the former were produced to 1 molecule of the latter (calc., 1·88 : 1). This was confirmed by repeating the complete series of experiments.

Preparation of Trimethyl Starch.

The methylation of starch may be carried to completion by continuing the methyl sulphate reaction in the manner now described. At the conclusion of the fourth methylation, when the reaction mixture was raised to 100° to destroy excess of methyl sulphate, the

liquid was saturated with salt. The hot liquor was then poured away, leaving the methylated starch adhering to the flask as a plastic mass. On adding hot water, a homogeneous syrup was gradually formed, and this was subjected directly to the next methylation, but at regular intervals the product was separated in a pure condition in order to ascertain with certainty the yields and analytical composition. The homogeneous aqueous syrup was therefore carefully neutralised with sulphuric acid and, after dilution with water, extracted by shaking with chloroform. The residue left on evaporation of the solvent was dried and taken up in dry chloroform, the solution being boiled for 20 minutes with charcoal and filtered hot. A hard, brittle material was left on removal of the chloroform and this, on boiling with ether, was converted into a white, amorphous powder. The treatment with ether eliminated traces of solvent and also removed a small quantity of depolymerised material. The following table indicates the progressive nature of the methylation :

No. of methylations	5	10	14	20	24
% OMe	35·5	39·6	41·4	43·2	43·7
$[\alpha]$ in $CHCl_3$ ($c = 1·7$) ...	+173·9°	+196·8°	+204·8°	+207·2°	+216·5°

At each stage, the carbon and hydrogen values were consistent with the methoxyl content, thus showing that the methylation proceeded without molecular rupture.

Starting from 32 g. of starch, the average yield after ten methylations was 15 g. and thereafter the experimental loss was regular, amounting to less than 0·4 g. per treatment. The final product (10 g., m. p. 143—146°) was a white powder less soluble in hot water than in cold, insoluble in ether, readily soluble in chloroform and in methyl alcohol. The aqueous solution was neutral, had no action upon Fehling's solution and gave no coloration with iodine (Found : C, 52·6 ; H, 8·0 ; OMe, 43·75. Calc. for trimethyl starch : C, 52·9 ; H, 7·8 ; OMe, 45·6%).

Hydrolysis of Trimethyl Starch.

Method (*a*). *Uncontrolled Hydrolysis.*—An 8% solution of methylated starch in methyl alcohol containing 1% of hydrogen chloride was heated at 100° for 24 hours and thereafter at 130° for 12 hours. The solution, which remained practically colourless, was neutralised with silver carbonate, filtered, taken to dryness, and the residue dissolved in ether. On filtering and evaporating, a colourless syrup remained (yield 94% of the theoretical amount) which was distilled under 0·1 mm. pressure. As the first drops of the distillate showed n_D 1·4551 and had OMe 51·4%, tetramethyl methylglucoside was definitely absent. The main fraction (yield

84%), which showed n_D 1·4583 and OMe 51·9%, consisted of trimethyl methylglucoside, a small, undistilled residue (OMe, 44%) being left in the flask. As under the conditions of the experiment the methylated glucoside was a mixture of α- and β-forms, it failed to crystallise (Found : C, 50·6; H, 8·4; OMe, 51·9. Calc. for trimethyl methylglucoside : C, 50·85; H, 8·5; OMe, 52·5%. $[\alpha]_D$ in methyl alcohol + 69·8° for $c = 1$).

The glucoside was thereafter hydrolysed by heating at 100° in 5% aqueous hydrochloric acid, the progress of the reaction, which was followed polarimetrically, displaying the characteristic double change in activity.

Time from start.	$[\alpha]_D$ for $c = 5$.	Time.	$[\alpha]_D$.
15 minutes.	+69·1°	3 hours.	+69·3°
45 minutes.	79·2	3 hours 45 minutes.	72·4
1 hour 45 minutes.	74·6	4 hours.	76·4
2 hours 30 minutes.	63·9		

The hydrolysis sugar, on isolation, crystallised immediately and completely, the m. p. before crystallisation being 70—80°, and, after purification from ether, 114°. This value remained unaffected on admixture with an authentic specimen of 2 : 3 : 6-trimethylglucose obtained from cellulose. The yield of crystalline sugar was 77% and the mother-liquors contained only a small quantity of uncrystallisable syrup. Contrary to expectation, this was not the isomeric 2 : 3 : 4-trimethyl glucose, as on conversion into the corresponding acetobromide and thereafter into trimethyl β-methylglucoside the product, after recrystallisation, melted at 57·5°. The compound also showed the correct mixed melting point and the standard specific rotation for 2 : 3 : 6-trimethyl methylglucoside.

Method (*b*). *Graded Hydrolysis.*—In this case, the hydrolysis was controlled so as to trace the stages of the reaction. The methylated starch (12 g.) was dissolved in 250 c.c. of methyl alcohol containing 1% of hydrogen chloride and boiled under a reflux condenser until the activity of the solution diminished to a minimum. This point was reached in from 8 to 9 hours and the product was isolated in the usual way. When distilled under 0·8 mm., 10·5 g. of pure trimethyl methylglucoside were obtained, whilst 2·8 g. remained undistilled. The distillate crystallised readily and, after purification from low-boiling petroleum, melted at 57·5° and showed $[\alpha]_D$ −29·3° in methyl alcohol for $c = 1$. When it was hydrolysed with 5% aqueous hydrochloric acid, the specific rotation altered from −25·4° to + 59·5° in 200 minutes, and crystalline 2 : 3 : 6-trimethyl glucose was ultimately obtained, the yield being 82%. A portion of the trimethyl methylglucoside failed to crystallise, but this material, which presumably contained the α-isomeride, was recovered from

the tile and hydrolysed separately. In this case also, 2 : 3 : 6-trimethyl glucose was the only sugar formed.

As already stated, 2·8 g. of non-volatile material were left undistilled when the hydrolysis of methylated starch was conducted as now described. The substance was a hard glass and consisted of depolymerised trimethyl starch (Found: C, 52·5; H, 8·0; OMe, 43%), as the composition remained unaltered but the solubility had increased while the specific rotation had diminished to + 86·9° in chloroform. Hydrolysis took place only when this material was heated for many hours at 130° with methyl alcohol containing 1% of hydrogen chloride, but the essential product was, as before, 2 : 3 : 6-trimethyl methylglucoside (OMe 41·6%; n_D 1·4590). This, in turn, was converted into crystalline 2 : 3 : 6-trimethyl glucose, the identity of which was confirmed by transformation into the corresponding β-methylglucoside. No trace of the 2 : 3 : 4-isomeride could be detected.

The authors gratefully acknowledge their indebtedness to the Carnegie Trust for a Research Scholarship and a Research Fellowship which enabled one of them to devote 4 years to the investigation.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, March 25th*, 1926.]

CXCVI.—*The Ultra-violet Spectra of Praseodymium, Neodymium, Samarium, Europium, and Erbium.*

By JAMES HENRY GARDINER.

VERY little work has been done in the photography of the ultra-violet absorption spectra of the rare earths, possibly on account of the rarity of the elements themselves and of the difficulty of photography.

Having in my possession specimens of many of the rarer elements in a state of purity, I thought that it would be of interest to place on record photographic reproductions of the absorption spectra of some of them. The five named above were found to give well-defined absorption bands in the region under examination; these spectra are shown together with a photograph of the light used to produce them. Photographs of this character lose much of their value unless care is taken to ensure uniformity in the conditions under which they are produced.

The spectrograph used is of novel design and has been constructed

purposely for this class of work; it consists essentially of a pair of quartz "Cornu" prisms with plano-convex collimating and object lenses. The "comparison spectrum" that is given in each case is put into position without any movement of the film by passing the radiation into the spectrograph through an aperture in a metal disc which is fixed in front of the slit; this disc has holes of different sizes and in different positions and it can be moved so as to confine the radiation entering the instrument to any one of them at will.

For this work it was necessary to use a very narrow slit, and it was essential for purposes of comparison that there should be no variation from the width in any of the spectra. A thick brass plate with a slot 2 mm. wide and 10 mm. long was made, and by the point, slot, and plane method it could be accurately fixed in the optical centre of the quartz train; upon the flat surface of the plate, jaws of hard steel with accurately ground edges were clamped at the determined width of 0·03 mm. This device of a slit with jaws that are immovable removes any possibility of accidental variation in its width such as would arise if it were adjusted by a screw.

All the photographs given are made with the same slit. The light used for the absorption spectra was produced by passing a high-tension current between electrodes of metallic uranium, producing a spark very rich in ultra-violet radiation. The spectrum of uranium has such a great number of lines so close together that, for the present purpose, it may be regarded as continuous.

At the top of each absorption spectrum and slightly overlapping it, is projected the spark spectrum of an alloy of the metals zinc, cadmium, mercury, and tin. These elements give well-defined lines of which the wave-lengths are known to a great degree of accuracy; their values given on each photograph make it possible, by means of a simple interpolation curve, to find the value of any of the bands shown. The wave-lengths of the approximate centres of the bands are given, although the photographs themselves are of more value than tables of wave-lengths and descriptions of the bands.

It was considered essential that the strengths of the solutions, *i.e.*, the amounts of the element present in each case, should be comparable or at least accurately known. The rarity of the materials available, and the obscurity of the chemistry of some of them, made this a matter of difficulty, but after some preliminary work it was decided to take the crystalline nitrates which have the general formula of $R(NO_3)_3,6H_2O$ as the basis of the solutions. These salts are easy to prepare and are soluble in water. As in some cases only a fraction of a gram of the element was available, it was decided to make all solutions from a weighed quantity of the

salt with ten times its weight of water. The solutions were in all cases put into a cell made from a glass cylinder, 20 mm. long, closed at the ends with plates of thin quartz.

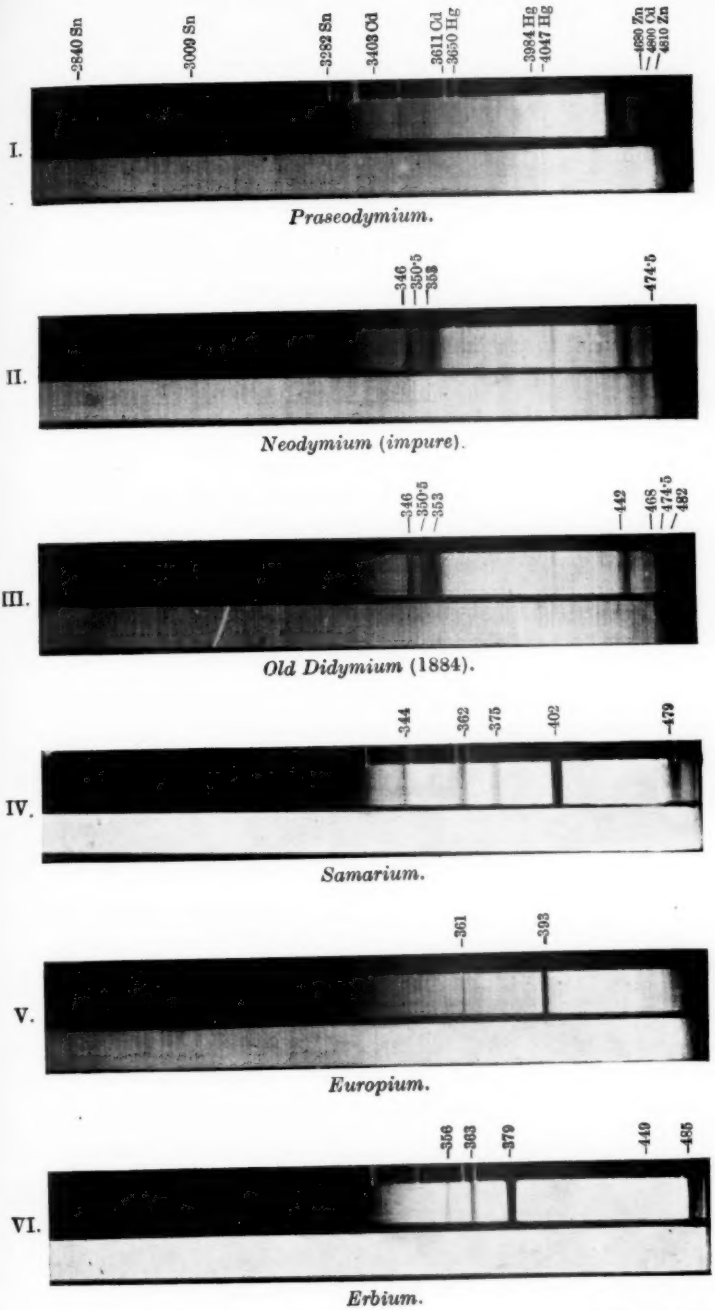
The procedure for the production of a photograph was as follows. By adjusting the aperture-disc so that the light passed into the upper part of the slit, an exposure was made to the light from the metallic alloy, and the disc was then rotated so as to present another opening slightly overlapping the first; the cell containing the solution was fixed in front of the slit, an exposure was given for 3 minutes to the uranium spark, the disc was again shifted so as to expose another part of the slit, and the solution was removed and another exposure given to the same light for the same time; this last exposure was considered to be advisable for reasons that will appear later.

In addition to the five elements that form the subject of this paper, 1 : 10 solutions of the nitrates of the following elements were made and their absorption spectra were photographed: lanthanum, ytterbium, gadolinium, terbium, thorium, cerium, and scandium. They did not show any absorption bands in the region under examination, *i.e.*, from 400$\mu\mu$ to the commencement of transmission, which in all cases was at about 350 $\mu\mu$. The elements giving absorption bands are described in the order of their atomic numbers.

Praseodymium.—This specimen was prepared some years ago by Thompson. The nitrate gives well-defined crystals dissolving easily in water to a brilliant green solution; the dried crystals, $Pr(NO_3)_3,6H_2O$, were used for the solution which was placed in the cell described above. The spectrum shows that it is quite free from neodymium and gives three well-defined bands at the least refrangible end; the approximate centres of the bands are 482$\mu\mu$, 468$\mu\mu$, and 442$\mu\mu$ (Fig. I).

Neodymium.—This material was obtained from the Welsbach Co. in the form of deliquescent crystals of pale rose colour; it was recrystallised by keeping the solution over sulphuric acid and gave good crystals of $Ne(NO_3)_3,6H_2O$. The spectrum (Fig. II) shows that the material is not quite free from praseodymium, but the three bands corresponding to this element are very faint; the bands of neodymium, however, are definite, and in this region of the spectrum are represented by a very faint and narrow band midway between the two least refrangible bands of praseodymium, at 474·5$\mu\mu$, and a well-defined group of three bands which do not appear to have been recorded hitherto; the wave-lengths of their maxima are approximately:

353 $\mu\mu$. Centre of the strongest part of a band having a broad wing on its least refrangible side;



Praseodymium.

Neodymium (impure).

Old Didymium (1884).

Samarium.

Europium.

Erbium.

[*To face page* 1520.]

350·5 μμ. Brightest edge of a band, fading off at the most refrangible edge;

346·7 μμ. Centre of the most refrangible band.

An interesting confirmation of the allocation of the faint band at 474·5 μμ to neodymium is seen by reference to Fig. III, which is the absorption spectrum of a 1 : 10 solution of the nitrate of a specimen of didymium prepared, in the form of a dark brown oxide, by Cleve in 1884 — some 12 months before Welsbach announced his discovery of the complex nature of the substance. It can be seen that all the bands of praseodymium and neodymium are visible, including the faint one at 474·5 μμ.*

Samarium. — Samarium nitrate forms yellow crystals of $Sm(NO_3)_3,6H_2O$. The spectrum of its solution is characterised by a very strong band having sharp edges and by four other broad, but faint, bands; there is also an indication of a fifth band, but it is too faint to measure. As the spectrum as a whole did not seem to correspond to the description given by Demarcay (*Compt. rend.*, 1900, **130**, 1185), other photographs of it were made using stronger solutions, but the character of the bands did not change. The measurements of the approximate centres of the bands are (Fig. IV):

First faint band: 479 μμ. Centre of dominant band: 402 μμ.

Centres of other faint bands: 375 μμ, 362 μμ, 344 μμ.

Europium.—This element is one of the rarest of the yttria earths. The oxide of the specimen under examination was of a faint cream tint, whereas it is said to be light pink. The spectrum shows a strong but narrow band with a very sharp edge on the more refrangible side, and one other faint but equally sharp band; the wave-lengths of the approximate centres are 393 μμ and 361 μμ (Fig. V).

Another specimen of this earth from an unknown source gave exactly the same spectrum.

Erbium.—The material from which the nitrate was prepared was a pink oxide prepared by Cleve in 1885. The wave-lengths of the absorption bands as determined by various observers vary considerably, but in this case there was one dominant band accompanied by four others that are all very faint; the wave-lengths of the approximate centres are as follows (Fig. VI):

A strong band at 485 μμ; a very faint band at 449 μμ.

* In discussing the spectrum of neodymium, J. F. Spencer ("The Metals of the Rare Earths," 1919) states that a band with a maximum at 469 μμ coincides exactly with one of the praseodymium bands and that this has led to the view that these substances contain an undiscovered element. The photographs of Cleve's old didymium and of the later praseodymium and neodymium fail to justify this view, as all the bands of the old element in this region of the spectrum are accounted for

The dominant band, sharp on the least refrangible side, at 379 μμ.

A very faint band, which is crossed by a strong uranium line (from the source of light), at 363 μμ.

A very faint line at 365 μμ.

This element is said to be slightly radioactive and a photographic experiment was therefore made : the oxide was filled into a tube closed at the end by a sheet of aluminium foil 0·04 mm. thick, which was fixed on a photographic plate so that the oxide was separated from the sensitive surface by the aluminium, and it was shut up in a dark box for 7 days. On developing, a faint but decided impression was obtained, where the oxide had rested. A similar experiment made with europia also gave an indication of radioactivity, but much more feebly.

[*Received, January 27th*, 1926.]

CXCVII.—*Extinction of Methane Flames by Diluent Gases.*

By Hubert Frank Coward and Francis John Hartwell.

In the course of an investigation on the influence of black-damp (a mixture of nitrogen and carbon dioxide) on the limits of inflammability of firedamp (methane) in air (Safety in Mines Research Board, Paper No. 19; London, H.M. Stationery Office, 1926), some new information has been obtained concerning the factors which determine whether or not a gas mixture is capable of self-propagation of flame. Volume for volume, carbon dioxide exceeds nitrogen in its extinctive action on flame—an effect which is generally attributed to the higher molecular heat capacity of the former. Argon, a gas of lesser heat capacity than either, proves to have less extinctive action. On the other hand, helium is much more extinctive of flame than argon, although the two have almost exactly the same heat capacities.

The limits of inflammability of methane, in various "atmospheres," composed of mixtures of air with one or other of the diluent gases, were determined in a vertical glass tube, 6 feet long and 2 inches in diameter. This tube was filled with an appropriate mixture, the lower end was then opened by sliding away a ground-glass joint and a small spirit-lamp flame was immediately passed across the aperture. The tube was sufficiently long to enable observers to judge whether a flame was self-propagating, for, if the mixture were incapable of continued self-propagation

of flame, the "cap" of flame formed above the source of ignition was extinguished within 2 feet of its passage up the tube.*

General Observations on the Flames.

The flame front, as the flame passed up the tube, was in all cases nearly hemispherical in shape, sometimes with a hollow, cylindrical extension of variable length. The blue flame front was followed by a red glow in all upper-limit mixtures, an evidence of some residual chemical reaction. The speed of propagation of flame in all limit mixtures, lower or higher, was remarkably constant at 22 to 23 cm. per second, except that the speed was somewhat higher when helium was the diluent used.

The flames in certain upper-limit mixtures vibrated rapidly when within 1 or 2 feet of the top of the tube. During these vibrations the flame, on occasion, was extinguished; however, when a pad of cotton wool was held loosely over the open end of the tube during the progress of the flame, vibrations were not observed and the normal shape of flame front and speed of propagation were obtained. Furthermore, the flame vibration started at the moment when the contraction due to cooling behind the flame became equal to, or just exceeded, the expansion due to new combustion; *i.e.*, at the moment of change, at the open mouth of the tube, from an outflow of gases to an inflow of air.

These observations afford a clue to an understanding of the causes of vibration in flames travelling along tubes, and will, it is hoped, form the subject of a later communication.

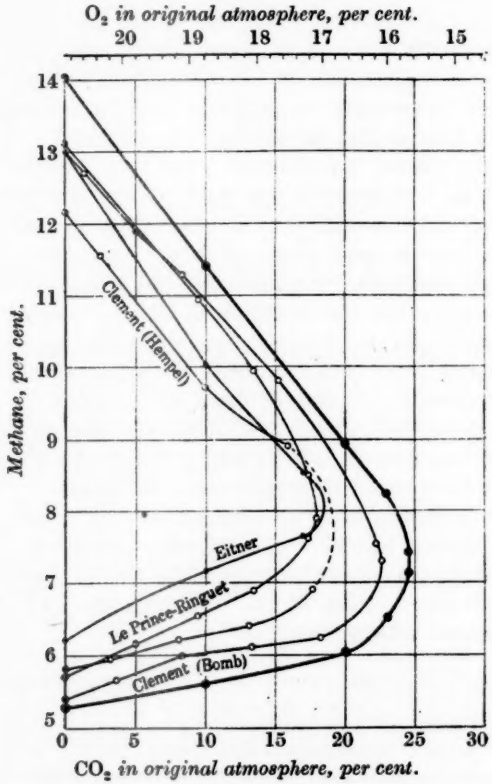
Limits of Inflammability of Methane–Air Mixtures in the Tube Used.—The limits in the circumstances described were 5·24% methane (lower) and 14·02% (higher).† These may be taken as accurate to 0·02%. Most of the results in the following sections were determined within 0·05%.

* In all the experiments recorded here, the gases were roughly dried by passage over calcium chloride, and contained less than 0·1% of moisture. They were at laboratory temperature up to the time of inflammation, and at laboratory pressure during the whole time of passage of the flame; the latter condition was secured by leaving the lower end of the tube open while the flame was passing up the tube. Ordinary variations in laboratory temperature and pressure have no measurable effect on the limits of methane–air mixtures (Mason and Wheeler, J., 1918, **113**, 45).

† When the gases were saturated with water vapour (1·9%) at the temperature of the experiment, the limits proved to be 5·22% methane (lower) and 13·54% (higher). These are the actual proportions of the gas present in the moist mixture; expressed (as usual from gas analyses) as percentages of the water-free mixture, they become 5·33 and 13·80. These last figures may be compared with earlier determinations which are, as a rule, expressed in this manner.

Influence of Carbon Dioxide on the Limits of Inflammability of Methane–Air Mixtures.—The heavy curve in Fig. 1 represents the limits of inflammability of methane in atmospheres composed of pure air admixed with the indicated amounts of carbon dioxide. The limits are narrowed as the amount of diluent gas is increased, until they meet when the atmosphere contains somewhat less than 25% of carbon dioxide. The increase in the lower limit is

FIG. 1.

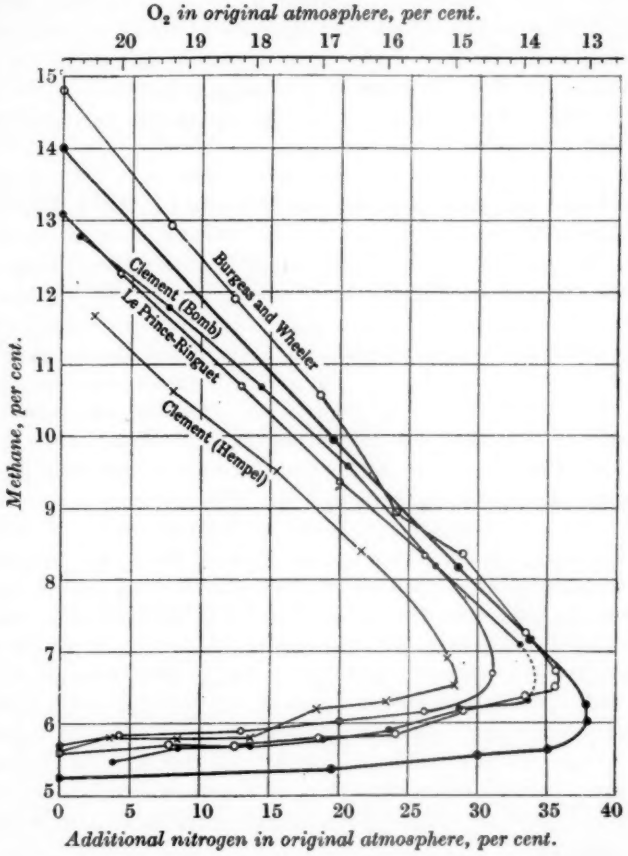


apparently due to the greater thermal capacity of the carbon dioxide, whilst the decrease in the higher limit is due to the combined effect of this and of the reduction in oxygen content of the atmosphere.

In the same figure are plotted results obtained by Eitner (*Habilitationsschrift*, München, 1902), Clement (*U.S. Bureau of Mines*, 1913, Technical Paper 43), and Leprince-Ringuet (*Compt. rend.*, 1914, **158**, 1999). They are not strictly comparable, however,

for the conditions of experiment were somewhat different in each case. Thus Eitner's and Leprince-Ringuet's refer to experiments on the downward propagation of flame in these mixtures, and Clement's to the propagation from a point near the top of a Hempel burette, or of a steel cylinder of some 3 litres capacity. The wider

FIG. 2.


O_2 *in original atmosphere, per cent.*
20 19 18 17 16 15 14 13
15 14 13 12 11 10 9 8 7 6 5
Methane, per cent.
Burgess and Wheeler
Clement (Bomb)
Le Prince-Ringuet
Clement (Hempel)
0 5 10 15 20 25 30 35 40
Additional nitrogen in original atmosphere, per cent.

limits indicated by our experiments, in which upward propagation was observed, were therefore to be expected.

Influence of Nitrogen on the Limits of Inflammability of Methane–Air Mixtures.—The heavy curve of Fig. 2 represents correspondingly the limits of methane in atmospheres composed of pure air admixed with the indicated amounts of nitrogen. The extinctive effect of nitrogen is considerably less than that of carbon dioxide, for the two limits do not coincide until about 38% of added nitrogen

is present in the atmosphere, as compared with 25% of carbon dioxide. These figures are almost exactly in the inverse ratio of the mean molecular heats (at constant pressure) of the two gases between room temperature and the flame temperature. Hence the difference in extinctive action is doubtless due to the difference in heat capacities of the two diluents. The lower limit shows a small but definite rise with increase in the proportion of nitrogen. As this diluent has the same heat capacity as air up to, and beyond, the flame temperatures of these experiments, this small rise must be ascribed to the reduction of the oxygen content of the atmosphere. The effect is masked by the operation of other factors when other chemically inert diluents are used.

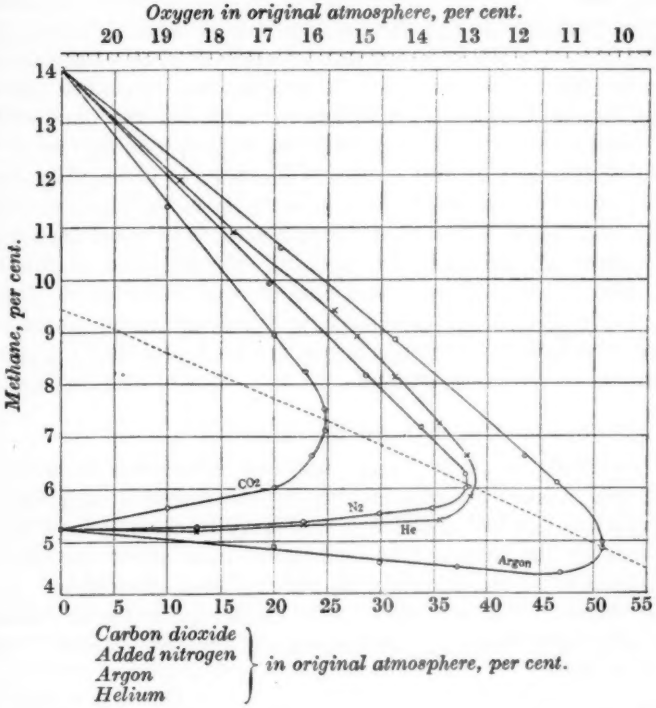
Fig. 2 shows also the results of Clement (*loc. cit.*), Leprince-Ringuet (*loc. cit.*), and Burgess and Wheeler (J., 1914, **105**, 2596). Here, again, the results are not closely comparable with the present series, for they were obtained under different conditions; but whereas for carbon dioxide–air "atmospheres" all the previous results showed narrower limits than those now presented, one set of the nitrogen results (Burgess and Wheeler's) shows, in general, greater values for the higher limits. Now those experiments were conducted in closed vessels, wherein the pressure rose considerably (several atm.) during the inflammation, and Mason and Wheeler (J., 1918, **113**, 45) have shown that increase of pressure increases markedly the higher limit of methane–air mixtures.

Influence of Argon on the Limits of Inflammability of Methane-Air Mixtures.—If the conclusions drawn from the experiments with atmospheres containing carbon dioxide and added nitrogen are correct, the lower limit of methane will have smaller values in atmospheres made from air and argon than in air itself, for argon has a lower heat capacity than air. Fig. 3 shows that such is the case, and that the minimum value of the lower limit is 4·40% of methane in an atmosphere composed of about 47% of argon and 53% of air, as compared with 5·24% of methane in the case of pure air. It requires nearly 51% of argon in admixture with air to produce an atmosphere which cannot form an explosive mixture with methane.

Influence of Helium on the Limits of Inflammability of Methane-Air Mixtures.—The heat capacity of helium is very nearly equal to that of argon and each, apparently, remains constant up to high temperatures. If, therefore, the extinctive effect of an inert gas is solely due to its thermal capacity and to its effect on the oxygen concentration of the atmosphere, the limits of methane should be identical in atmospheres composed of ordinary air mixed in one case with argon and in another case with an equal volume

of helium. Fig. 3 shows the action of helium, which, contrary to expectation, is markedly more extinctive of methane–air flames than is argon.* From a detailed consideration of the physical differences between these two gases, we ascribe the superior extinctive action of helium to its greater thermal conductivity,† which is more than eight times that of argon, at laboratory temperatures. We have no experimental information about the temperature coefficients of the conductivities of such mixtures as we are using,

FIG. 3.


Oxygen in original atmosphere, per cent.
20 19 18 17 16 15 14 13 12 11 10
Methane, per cent.
14 13 12 11 10 9 8 7 6 5 4
CO2
N2
He
Argon
0 5 10 15 20 25 30 35 40 45 50 55
Carbon dioxide
Added nitrogen
Argon
Helium
in original atmosphere, per cent.

* A mixture of composition $CH_4 + 2O_2$ was diluted with (*a*) argon, (*b*) helium, until it was no longer inflammable. The limit mixtures contained (*a*) 3·95, (*b*) 5·00% methane. For *downward* propagation of flame in a tube of the same size, firing from near the open end, similar results were obtained; in an atmosphere composed of 80% of air and 20% of inert gas, the lower limits were (*a*) 5·50, (*b*) 5·75% methane when the inert gas was (*a*) argon, (*b*) helium.

† The thermometric conductivity, or diffusivity, which is equal to the thermal conductivity divided by the specific heat (C_p) of unit volume, is the function which would have to be used in a quantitative analysis of the phenomena of flame transmission. In the present argument, the terms may be used interchangeably.

but some indication is given by Stafford's work (*Z. physikal. Chem.*, 1911, **77**, 66) on the temperature coefficients of the conductivities of air and carbon dioxide separately, and Weber's work (*Ann. Physik*, 1917, **54**, 481) on the conductivities of some mixed gases at laboratory temperatures. It seems highly probable that the thermal conductivity of a gas mixed with helium will be greater than that of a corresponding mixture with argon, and that this will be true at the somewhat high temperatures of the flames in limit mixtures. At first sight, it is surprising that the higher thermal conductivity of helium should be responsible for its greater extinctive action; but if the propagation of flame is due to conduction of heat, then at either zero or infinite values of the thermal conductivities flame would not be propagated. Between the two values, zero and infinity, an optimum value for the conductivity must obtain; so it is evident that the higher conductivity of the helium mixtures may well be less favourable to flame propagation in limit mixtures than the lower conductivity of the argon mixtures.

This conclusion is in good accord with, and receives support from, observations made by Coward, Cooper, and Jacobs (J., 1914, **105**, 1069). They found that it was much more difficult to ignite, by the electric discharge, mixtures of various gases when diluted with helium than when argon was used, and they interpreted the results in a similar manner.

General Discussion.

If, therefore, it is probable that the differences between the argon and helium curves are due to the different thermal conductivities of the two gases, it is necessary to consider how far the discovery of the influence of this factor may affect our previous conclusions as to the influence of varying heat capacities.

The thermal conductivities at 0° of the gases under consideration are (Glazebrook, "Dictionary of Applied Physics," 1922, vol. 1, p. 459)

Helium	$32{\cdot}7 \times 10^{-5}$	Nitrogen	$5{\cdot}14 \times 10^{-5}$
Argon	3·85 „	Air	5·22 „
Carbon dioxide	3·25 „		

The difference in thermal conductivity between carbon dioxide and nitrogen (1·9 units) seems far too small to account for the difference in extinctive action between these two gases, for there is about the same difference in extinctive action between helium and argon for a very much greater difference in thermal conductivity (28·9 units). We may therefore adhere to our earlier conclusion that the thermal capacity factor is predominant in determining the relative extinctive effects of two diluent gases, but we may

add that, when a gas of very different thermal conductivity is introduced, then this factor will become important.

A Connexion between Lags on Ignition and Dilution Limits.—When inflammable mixtures of methane and air are heated to any temperature above their ignition temperature, a distinct interval of time must elapse before inflammation is observed. The relative ease of ignition of methane–air mixtures containing the various diluents used in this research, as indicated by their relative "lags" on ignition, might be regarded as a governing factor in determining the order of the limits. Determinations of such "lags" have recently been made in the Safety in Mines Research Board Laboratories in connexion with another research which will be published shortly. At the temperature of the flames in limit mixtures (calculated to be between 1100° and 1400°) the lags, under the conditions of experiment, were too short to be measured for comparative purposes, but at 950° they were reasonably long, and are shown for 6% methane mixtures in atmospheres containing 30% of diluent. The same table also shows the limiting proportion of the diluent which is completely extinctive at normal temperature and pressure.

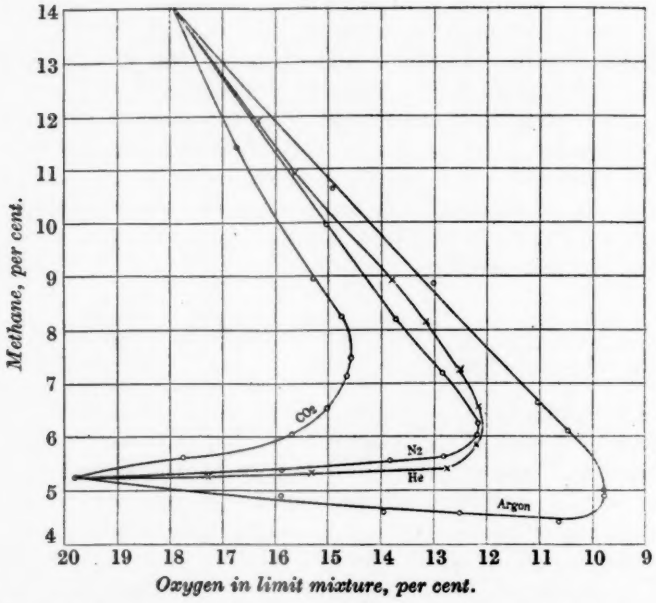
Diluent.	Carbon dioxide.	Nitrogen.	Helium.	Argon.
Lag (seconds)	0·275	0·25	0·22	0·19
Limiting proportion (%) ...	25	38	39	51

It is tempting, perhaps, to explain the relative extinctive effects as being the result of the relative lags; but it is more reasonable to regard the lags as determined largely by the same factors as determine the extinctive effects, namely, thermal capacities and thermal conductivities, because the lag is generally explained as being the period in which the gas mixture is heating itself, by partial combustion, to the temperature of rapid reaction. Other circumstances being equal, the lag must therefore be shorter in the presence, not only of inert gases of lower thermal capacity, but also of gases of lower thermal conductivity.

The Most Inflammable Mixture of Methane and Air.—The broken line in Fig. 3 is the locus of mixtures in which the ratio between methane and oxygen is exactly that required for complete combustion, $CH_4 : 2O_2$. This line runs through the "noses" of the limits curves, and therefore, from this point of view, the most inflammable of all mixtures of methane and oxygen is that which burns completely to carbon dioxide and water. This is also the mixture in which the speed of uniform movement of flame is greater than in any other mixture of methane and oxygen (Payman, J., 1920, **117**, 48). On the other hand, the detonation wave is pro-

pagated more rapidly in mixtures in which the methane content exceeds that required for complete combustion (Dixon, *Phil. Trans.*, 1893, **184**, 97); in this case, the heat of reaction is evidently subordinated by those physical properties of the explosive mixture which govern the rate of transmission of a disturbance like a sound wave. Moreover, the speed of uniform movement of flame in methane–*air* mixtures reaches its maximum when the proportion of methane is somewhat higher than the theoretical amount for complete combustion (Wheeler, J., 1914, **105**, 2606), whilst mixtures

FIG. 4.



containing an excess of air are more readily ignited by a heated surface or by an electric spark.

Test of the "Limits Generalisation" of Payman.—Le Chatelier (*Ann. Mines*, 1891, **19**, 388) gave a formula which enabled the lower limit in air of a mixture of two inflammable gases to be calculated from the observed limits of the separate gases. This formula was put in more general form by Coward, Carpenter, and Payman (J., 1919, **115**, 27) and was shown to apply to lower and higher limits, in air, of mixtures of hydrogen, methane, and carbon monoxide, and of coal gas. It expressed in mathematical terms the statement that "lower-limit air mixtures, if mixed in any proportions, give rise to mixtures which are also at their lower limits."

Payman (J., 1919, **115**, 1436) gave the statement a still wider form which applies to cases in which the atmosphere is not air: "All mixtures, in any proportions, of limit mixtures remain limit mixtures . . . provided that all of the limit mixtures are of the same kind, that is to say, all lower-limit or all upper-limit mixtures." This statement is tested by the present research for atmospheres which contain large quantities of carbon dioxide, excess nitrogen, argon, and helium. It holds good in each case when mixtures represented by points on the straight part of a curve (Fig. 4) * are considered; it fails when points on the curved parts are considered, and the extent of the failure is represented by the greater or lesser curvatures at the point chosen. The generalisation is therefore fairly accurate for methane in atmospheres composed of air mixed with the inert gases named, except when applied to those mixtures the composition of which approaches the point where the lower and higher limits coincide.

Results.

Limits of inflammability of methane in atmospheres composed of air mixed with various diluent gases, observed in a vertical tube 2 inches in diameter, upward propagation of flame, the lower end of the tube being open; gases at atmospheric temperature and pressure.

Diluent in "atmosphere" %.	Limits of inflammability.		Diluent in "atmosphere" %.	Limits of inflammability.	
	Lower.	Higher.		Lower.	Higher.
Nil.	5·24	14·02	Nitrogen.		
			19·6	5·39	—
Carbon dioxide.			19·8	—	9·97
10·0	5·61	11·40	28·5	—	8·18
20·0	6·07	8·95	30·0	5·55	—
23·0	6·57	8·23	33·8	—	7·18
24·5	7·12	7·47	35·0	5·63	—
Argon.			37·9	6·01	6·26
20·0	4·91	—			
20·6	—	10·62	Helium.		
29·9	4·60	—	12·8	5·27	—
31·3	—	8·85	16·0	—	10·90
37·2	4·48	—	22·8	5·35	—
43·6	—	6·62	25·6	—	9·40
46·6	—	6·11	27·7	—	8·93
46·9	4·40	—	31·3	—	8·14
50·8	4·87	—	35·3	—	7·27
50·9	—	4·99	35·5	5·40	—
			38·2	—	6·56
			38·5	5·83	—

* The replotting of the experimental values on a different basis from that of Fig. 3 is necessary to exhibit the approach to a rectilinear character which tests the validity of the generalisation.

Summary.

1. The limits of inflammability of methane in atmospheres composed of air mixed with (*a*) carbon dioxide, (*b*) nitrogen, (*c*) argon, and (*d*) helium have been determined, and the factors which are mainly responsible for the extinction of flame have been elucidated. They are (1) the reduction of oxygen content by the diluent gas, (2) its thermal capacity, and (3) its thermal conductivity. An exact treatment of the subject would therefore demand a knowledge of the thermal conductivities of certain mixed gases up to high temperatures (say, 1000° to 1500°). Such data are not at present available.

2. The thermal capacity effect of the diluent gas is marked in the case of argon; the lower limit of methane in the conditions described is reduced from 5·24% in air to 4·40% in an atmosphere composed of 47% of argon and 53% of air, and is further reduced to 3·95% in an atmosphere composed of argon with just sufficient oxygen to burn the methane completely.

3. The thermal conductivity effect is marked when a comparison is made between the limits in atmospheres composed of air to which has been added argon, on the one hand, or helium on the other.

4. The "limits generalisation" of Payman holds fairly accurately over the whole range of mixtures investigated, except near the point at which the lower and higher limits meet.

5. Of all mixtures of methane and oxygen, that represented by the proportions $CH_4 + 2O_2$ is the last to become non-inflammable as inert gases (nitrogen; or nitrogen with carbon dioxide, argon, or helium) are added in increasing amount.

6. There is a parallel between the "lags" on ignition and the dilution limits of such mixtures as we have used. It is suggested that both are dependent on the same factors, in the case of any one inflammable gas.

This work has been carried out at the suggestion and under the general direction of Professor R. V. Wheeler. We desire to express our appreciation of the able manner in which Miss E. H. M. Georgeson and Mr. G. W. Jones, at Sheffield and Pittsburgh, respectively, have assisted us in this investigation, and to acknowledge the permission granted by the two organisations concerned to publish this work.

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BUREAU OF MINES EXPERIMENT STATION,
PITTSBURGH, U.S.A. [*Received, April 15th*, 1926.]

CXCVIII.—*Periodic Phenomena at Anodes of Copper and Silver.*

By Ernest Sydney Hedges.

The only case of the periodic dissolution of a metal under anodic polarisation which has received systematic examination is the periodic passivity of iron. A complete series of references to this and other periodic electrochemical phenomena is to be found in a paper by Hedges and Myers (J., 1925, **127**, 1013). In that paper, periodic electrochemical phenomena were classified in two groups: (*a*) systems which are capable of furnishing a periodic current, and (*b*) systems which behave periodically on electrolysis; and the experimental portion was devoted to section (*a*). The present work is an experimental investigation of section (*b*).

The reactions differ in several important respects from the experiments of Hedges and Myers (J., 1924, **125**, 604; 1925, **127**, 445) on the periodic dissolution of metals in various reagents in absence of applied current. For example, a metal which liberates hydrogen when dissolving in an acid may undergo electrolytic dissolution without production of any gas, or at suitable current densities oxygen may be evolved at its surface. The absence of gas evolution enables diffusion effects, supersaturation, and film formation to play important rôles, and the system may be further complicated by polarisation, overvoltage, etc.

It is not surprising, therefore, that the electrolytic periods described in the present paper should differ in some fundamental respects from the periodic phenomena in purely chemical reactions. Thus, the periods formerly described were (1) dependent on the presence of a third component, (2) dependent on a peculiar physical state of the metal, (3) increased in frequency linearly with the rate of dissolution, and (4) lengthened enormously or stopped altogether by catalytic poisons. On the other hand, the electrolytic periods now described are (1) independent of a third component, (2) independent of the state of the metal, (3) decreased in frequency with increasing rate of dissolution, and (4) unaffected by catalytic poisons.

There are reasons for supposing, however, that the fundamental causes of these manifestations of periodicity are not essentially different.

Experimental.

Apparatus.—The electrolysis was conducted in a wide-necked glass bottle of 200 c.c. capacity, the amount of solution used in each experiment being 100 c.c. The electrodes were of pure electro-

lytic metal sheet, 4 cm. × 2 cm., and were supported by nickel rods, to which they were fastened by means of a nickel screw, a small hole being drilled near the end of each electrode. A length of only 3 cm. of electrode was immersed in order to keep the nickel well clear of the solution. The metals were approximately 0·5 mm. thick, and the effective area of each may therefore be taken as 12 sq. cm. The distance between the electrodes was 2 cm. A rubber bung, closing the reaction vessel, served to carry the electrode supports and the glass tubes for stirring the solution. Except in experiments where it was undesirable, the solutions were vigorously stirred during electrolysis by a stream of air previously freed from carbon dioxide. The reaction vessel was immersed in a thermostat at 30°, except in those experiments where other temperatures are indicated.

The source of current was a battery of twelve Edison storage cells of large capacity. The current passing through the circuit was read directly on an ammeter placed in series with the cell, and the *P.D.* between the electrodes was measured by a voltmeter of suitably high resistance placed across the electrode terminals. Both were quite dead-beat instruments. The course of the electrolysis was followed by taking readings of the voltmeter every 15 seconds, or, if necessary, every 5 seconds.

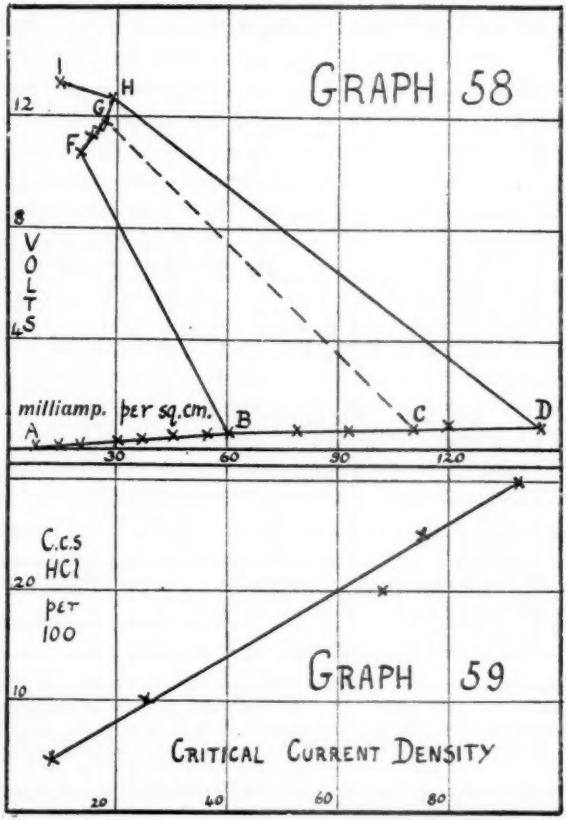
(1) *Copper Anode.*

Electrolysis of some Chloride Solutions.—When fairly strong solutions of hydrochloric acid are electrolysed between copper electrodes at low current densities, copper passes into solution at the anode as cuprous chloride. As a rule, this may be seen on the metal as a white coating which, however, does not appreciably impede the electrolysis. In the absence of atmospheric oxygen, no cupric salt is formed. At high current densities, a film which appears to be cuprous oxide forms over the metal; this film is highly resistant and the current passing falls to a low value; the electrode still dissolves, but a small portion of the current is employed in the liberation of oxygen, a few bubbles of which rise from the anode. At intermediate current densities the two effects alternate. The seat of this phenomenon is the anode, for the effect continues if platinum be substituted for the cathode, but not if the anode be changed for another metal. Further, the anode undergoes a visible periodic change.

The Current Density–Potential Curve.—Graph 58 (Fig. 1) shows the effect of gradual increase in current density in the electrolysis of hydrochloric acid, containing 25 c.c. of acid (*d* 1·16) in 100 c.c., using a copper anode and a platinum cathode at 20°. For values

below 60 milliamp. per sq. cm. the potential rises slowly along the line AB: cuprous chloride is formed at the anode and dissolves in the hydrochloric acid, and at the cathode copper is deposited and hydrogen evolved. At the value corresponding to B the potential oscillates in regular periods between 0·55 and 10·6 volts, and simultaneously the current fluctuates between 60 and 20

FIG. 1.

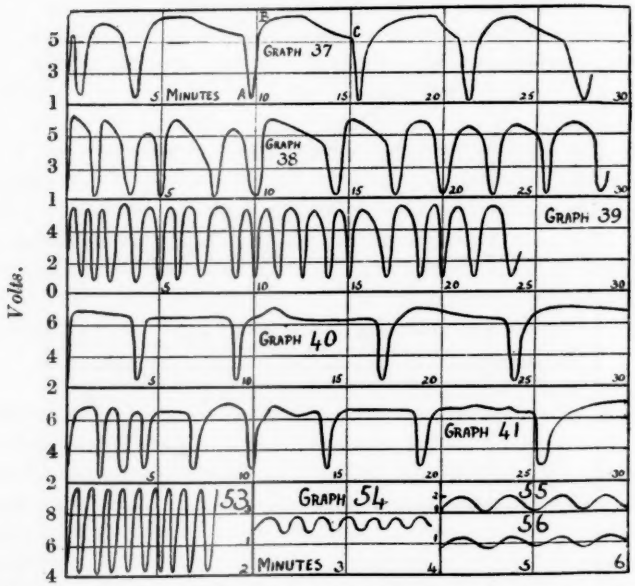


milliamp. per sq. cm. The region of regular oscillations continues as the current density is increased along BD to the value 145 milliamp. per sq. cm., the amplitude here being from 1·0 to 12·7 volts. At an intermediate point C, the values of current density and potential oscillate between points C and G. At current densities greater than 145 milliamp. per sq. cm., the potential immediately rises (the current falling) to a voltage corresponding to H, at which it remains constant. Further attempts to increase the current are

unsuccessful, for the film over the anode becomes more and more resistant and the effect is actually to decrease the current still further, along the line HI. The electrode, therefore, exists in one state along AB, in another state at H, and the area BFHD marks a region of instability where the electrode oscillates regularly between the two states.

The point B represents the critical current density required to produce periods. The value of this increases with the concentration of the hydrochloric acid and with rising temperature. The

FIG. 2.



The amplitude in Graphs 37—41 is about half of that indicated in Graph 58. This is because half the number of cells was used in these experiments. When the highly resistant film forms, the voltmeter records almost the total E.M.F. *of the battery, the resistance of the rest of the circuit being relatively small.*

critical current densities for a series of solutions containing from 5 to 30 c.c. of hydrochloric acid per 100 c.c. of solution electrolysed between two copper electrodes have been determined, and Graph 59 indicates a direct proportionality between critical current density and concentration.

The Nature of the Phenomenon.

The periodic changes in current and potential are accompanied by visible periodic changes at the anode. This is best described by reference to one of the waves on Graph 37 (Fig. 2). Simul-

taneously with the sudden rise in the potential (AB), there sweeps *up* the metal a very thin, dark grey film. The current slowly increases until the point C is reached. Then the potential rapidly resumes its initial low value and a white film sweeps *down* the metal. There is an interval of a fraction of a second between the drop in potential and the appearance of the white film. Careful observation shows that simultaneously with the drop in potential the smooth dark grey film breaks up into a rough red-brown film having the appearance of cuprous oxide. The transformation to the white film is almost immediate. The series of changes is repeated in each successive wave. The first film has the appearance of cupric oxide rather than cuprous, but there is doubt in assigning a composition to so thin a film. It is believed to be a form of cuprous oxide, for it changes directly into ordinary cuprous oxide and gives cuprous chloride by reaction with hydrochloric acid: further, no cupric salt is produced in the reaction. The white film is undoubtedly cuprous chloride.

It has been observed that wherever deposition of a film occurs in electrolysis, this starts at the sides and lower part of the electrode and travels up the electrode in the form of a **U** of diminishing concavity. This seems to be due to the concentration of current density at the corners and edges of the electrode and accounts for the manner in which the dark oxidic film travels up the anode. The downward sweep of the cuprous chloride film has been traced to the flow of hydrochloric acid down the electrode due to the downward fall of the reaction products, which is observed even when the solution is stirred. By allowing a stream of air bubbles to impinge on a point near the bottom of the anode, the reaction products can be washed upwards, and under these conditions the cuprous chloride film travels upwards also; but the oxide film could not be made to travel downwards.

The phenomenon is not affected by moderate rates of stirring, but when the solution in the vicinity of the anode is stirred very vigorously the frequency of the periods is increased or the potential may even remain constant at the low value. In the latter case, periodicity recurs on increasing the current density. Thus the phenomenon may be localised by directing a stream of air bubbles on a point about half-way up the electrode. In this case, the small area of metal affected by the rapid stirring exhibits rapid black and white flashes, while the main part of the electrode performs its slow periods unhindered. The voltmeter records curves showing short waves superimposed on the long waves.

These effects, which could be controlled by the air used for stirring, suggested that the phenomenon was due to oxidation and

probably to an oscillation of the reaction product between the cuprous and cupric states. Experiments were therefore performed in which the solutions were stirred by a stream of hydrogen bubbles. The effects of localised stirring were the same as with air and in this case no cupric salt was formed. Further, the periods were produced when the hydrochloric acid contained 1% of sulphurous acid. Separate experiments showed that a copper anode did not give periods in 1% or 5% sodium hydrogen sulphite solution alone. It may be noted that in the presence of sulphurous acid a somewhat higher critical current density was required.

Observations taken on interrupting the periods have given a clue to their nature. If the circuit be broken or the electrodes be short-circuited while the high *P.D.* exists, the cuprous chloride film immediately forms over the anode. In this case, it does not travel down the metal, but appears simultaneously over the whole area. If the circuit be completed again directly, the oxide film is reinstated immediately and the *P.D.* again rises. When an interval of 1 or 2 seconds elapses before the circuit is remade, the film does not form again for a few seconds. By breaking and making the circuit several times in succession, preferably in an unstirred solution, the cuprous chloride film does not form when the *P.D.* drops, but, instead, the oxide film turns to the red colour and the white film appears when the circuit is again made; it is quickly followed by the oxide film, the *P.D.* rising once more.

These facts suggest the following interpretation. The critical current density is such that chlorine ions are discharged more rapidly than they can be replaced by diffusion; at a certain moment, therefore, hydroxyl ions are discharged and a highly resistant oxide film forms over the metal, causing the *P.D.* to rise to a high value. This film is unstable (as will be shown independently later) and changes to a stable state of relatively low resistance, the change being indicated by the change in colour and surface of the film. This is immediately followed by reaction with the chlorine ions, which have been accumulating through diffusion, to form cuprous chloride. When the current is broken for a fraction of a second, the oxide film (which is only stable at the high potential) immediately reacts with the available chlorine ions and then rapidly forms again as these become scarce. When, however, the circuit remains open for a few seconds, the chlorine ions have time to diffuse towards the anode and, on making the circuit once more, a few seconds elapse before the oxide film forms. By repeating this process several times in rapid succession, the solution in the immediate vicinity of the anode can be so deprived of chlorine ions that breaking the circuit causes the highly resistant film to change to

the red stable state, in which form it persists for some little time; but closing the circuit causes it to react to form cuprous chloride.

Direct evidence of the instability of the highly resistant oxide film is gained by observing the effect of partially lifting the anode out of the solution when in the state represented by H in Graph 58. When this is raised 1 cm., the change to the stable state is observed to take place in the upper part of the electrode and a well-defined ridge forms about 0·5 cm. above the surface of the solution, marking the boundary between the stable and unstable forms. Each time the electrode is progressively raised, a further area remote from the solution undergoes the change and a new boundary forms, below which the grey film persists. This boundary marks the extent of the electrode which is under the influence of the high current density. The highly resistant film is stable, then, above a current density of 145 milliamp. per sq. cm., and its metastability between the values 60 and 145 milliamp. per sq. cm. is the cause of the periodicity.

Having deduced the mechanism of the process from direct experimental observation, it is necessary to show how this is supported by a study of the effect of varying the conditions of reaction.

Effect of Conditions.

(a) *Current Density.*—For any given concentration, the frequency of the periods decreases greatly with increasing current density. This is illustrated by the following values in a solution containing 25 c.c. of hydrochloric acid per 100 c.c.

Milliamp.	58	72	86	117
Min.	1·25	2·0	4·25	9

Such a result is to be expected, for the high current density (1) more rapidly exhausts the anolyte of chlorine ions, and (2) stabilises the resistant film.

(b) *Temperature.*—At a given current density, the frequency of the periods increases with rising temperature. This effect takes place in a particular way, however. The lower part of the curve (Graph 37) is unaffected and only the portion BC is shortened. On raising the temperature still higher, the amplitude AB is gradually reduced until finally the effect dies out and the potential remains constant at the low value. Periodicity can then be recovered by increasing the current density. Thus, a system at 20° under a current density of 80 milliamp. per sq. cm. gave an amplitude of 5·7 volts, the high *P.D.* lasting for 120 seconds; at 35°, the amplitude was 4·8 volts, lasting for 30 seconds; at 45°, 2·8 volts for 10 seconds; at 55°, 0·3 volt for 5 seconds. In each case, the low *P.D.* had a duration of 30 seconds.

Above 60°, no oscillation was perceptible, but by increasing the current density to 108 milliamp. per sq. cm. variations between 0·4 and 0·8 volt were recorded; at 126 milliamp. per sq. cm. the *P.D.* oscillated between 0·5 and 4·1 volts.

Thus, the effect of raising the temperature is to decrease the stability of the resistant film, and in every way it acts in an opposite sense to increasing current density : the two are mutually antagonistic.

(c) *Concentration.*—Graphs 37, 38, and 39 (Fig. 2) show that for a fixed temperature and current density (in this case 30° and 71 milliamp. per sq. cm.) the frequency of the periods increases with increasing concentration of hydrochloric acid. The rate of dissolution of the metal remains the same in the three cases. This result would be anticipated from the explanation advanced, for the anolyte is with greater difficulty depleted of its store of chlorine ions. The linear relation between the critical current density and the concentration of solution is likewise compatible. The wave-length gradually increases during the course of the electrolysis. This is due partly to decrease in concentration of the chlorine ions and partly to formation of cupric chloride through oxidation by the air-stream. Direct addition of 1% of cupric chloride was found to double the length of the waves.

(d) *Rate of Stirring.*—This factor is inconsiderable when the solution is kept in circulation without violently disturbing the solution at the anode. When the stream of bubbles is allowed to travel up the anode the frequency of the periods is increased and the critical current density raised. This is due to the rapid replenishing of the depleted chlorine ions, causing the effective concentration to be higher.

(e) *Addition of Agents.*—Addition of a reducing agent, such as sulphurous acid, served to shorten the periods and to raise the critical current density. On the other hand, oxidising agents such as hydrogen peroxide lengthened the periods. A system with a normal period of 4·25 mins. produced periods of 4·5 mins. after addition of 1 c.c. of 20-volume hydrogen peroxide, 6·5 mins. in the presence of 2 c.c. of hydrogen peroxide, and 10·5 mins. with 4 c.c. Addition of 0·5% of potassium cyanide or 0·5% of formaldehyde failed to " poison " the oscillations. The presence of 0·02% of gelatin did not affect the phenomenon. No difference could be observed between the behaviours of cold-rolled and well-annealed copper.

The periodic phenomenon takes place in solutions of other chlorides in similar circumstances and the same general effects are observed. Thus, equally well-marked periods are produced when

10% or 5% ammonium chloride is used for the solution to be electrolysed. Graph 40 (Fig. 2) illustrates the periodic dissolution of a copper anode in 5% ammonium chloride solution. Graph 41 records a similar experiment using 5% sodium chloride solution. In the latter case, the reaction product is mainly cuprous oxide, which is insoluble but does not adhere to the electrode; it soon causes the solution to become opaque, thus preventing observation. Long periods are obtained when 5% cupric chloride solution is used as the electrolyte.

Electrolysis of Potassium Cyanide Solutions.

Anodes of copper in 2·5% and 5% solutions of potassium cyanide rapidly become enveloped by a golden-green film which readily dissolves in the electrolyte on breaking the circuit. This is generally described as a basic cyanide. At certain current densities, the voltmeter needle trembles violently and occasionally executes rapid fluctuations of about 1 volt. The phenomena are much more definite in a 10% solution. At low current densities, no film forms over the anode and the copper dissolves as potassium cuprocyanide. When the current density is raised to 59 milliamp. per sq. cm. a dark grey oxide film sweeps up the metal and the *P.D.* between the electrodes rises from 1·6 to 2·7 volts. After a few seconds, the dark film gives place to a white film, presumably of cuprous cyanide, which travels down the metal, and the *P.D.* resumes its former value. The two states oscillate thereafter in regular periods.

In every respect this phenomenon is similar to the periodic electrolysis of chloride solutions, and the oxide film reacts towards interruption of the current just as in the former cases. It is therefore a logical deduction that the mechanism is precisely similar. The limits of the conditions favouring periodicity in the cyanide solutions are, however, very much narrower than in the chloride solutions. If a current density–potential curve similar to Graph 58 be constructed for a cyanide solution, the region of instability BFHD is very short and is indeed easily overshot, the electrode often going straight from the state represented by B to that represented by H. It is only by increasing the current density cautiously that the intermediate oscillating condition can be realised in this system.

Another point differentiates the systems. On further increasing the current density to 86 milliamp. per sq. cm., a pale green film permanently covers the anode. At this stage, cuprous cyanide is being formed more quickly than it can dissolve in the potassium cyanide solution. The onset of this film is marked by a rise in

potential from 3·6 to 6·2 volts, after which a second series of oscillations ensues. These are most diverse in character, varying in amplitude from 0·1 to 6·0 volts and in wave-length from 0·1 to 5·0 seconds. Occasionally they become regular for some few minutes, after which the voltmeter needle behaves in an erratic manner, violent trembling being interspersed with sudden momentary darts up to a high value. Current densities exceeding 140 milliamp. per sq. cm. are beyond the region of periodicity in the cyanide film, but the erratic behaviour may be repeated by again lowering the current density. Since no change can be observed in the film in this second series of oscillations, there are as yet no data to afford an explanation. Analogy would suggest that the cyanide is first deposited in an unstable form at the high current density employed.

The phenomena are even better marked in 20% potassium cyanide solution. Illustrations of periodicity in the oxide film and of regular periods in the cyanide film are shown in Graphs 54 and 53 (Fig. 2), respectively. All these experiments on cyanide solutions were conducted at 20° because of the high frequency, and the solutions as a rule were not stirred in order to avoid loss of hydrogen cyanide. Control experiments in stirred solutions gave similar results, except that somewhat higher current densities were required in every case.

Electrolysis of Other Solutions.

Sulphuric Acid.—Investigations were carried out at intervals of 10% over the concentration range 100—10%, and also at 5, 2, and 0·5% (expressed as % by volume of acid, *d* 1·84). With concentrations above 50%, very little current would pass, the *P.D.* rapidly rising to a high value. After a time, cupric sulphate could be seen as crystals on the anode. Electrolysis followed a normal course below 10%, and at intermediate concentrations the potential rose to a high value at a certain critical current density. This was followed by a partial fall in the 40, 30, and 20% systems, but in no case was a periodic effect produced. It is probable that the highly resistant film was in this case copper sulphate. In the more dilute solutions (below 10%), some loosely adherent cupric oxide was always formed at high current densities. The 40% system was examined over a temperature range of 20° to 75°. Between these limits the critical current density increased from 58 to 138 milliamp. per sq. cm., but periodic effects were not produced.

Nitric Acid.—The concentrations examined were 10, 5, 2, and 0·5% (by volume of acid of *d* 1·42). In all these cases, the electrolysis pursued a steady course over the whole range of current densities. At the end of each experiment, the anode was covered

with a slimy, black deposit, probably of cupric oxide, which did not increase the resistance of the system. In one experiment with 5% nitric acid, continuous oscillations with a 30-second period between 0·8 and 1·0 volt were observed, using a current density of 36 milliamp. per sq. cm. Subsequent attempts to repeat this have failed. It is possible that the periods were due to some accidental circumstance, or that their range of existence was very narrow.

Sodium Hydroxide.—Solutions of concentrations graded from 8% to 0·4% were used. With the 8% solution at current densities below 5 milliamp. per sq. cm. a resistant film of cupric oxide slowly formed on the anode, the *P.D.* rising from 1·2 to 2·3 volts, at which oxygen was evolved. The film disappeared on increasing the current further and a greenish-yellow substance could be observed going into solution. Periods were not observed in any of these systems or in concentrated solutions of ammonia. A large number of mixtures of solutions of caustic soda and ammonia were also tried without success.

Miscellaneous.—Solutions of the following compositions were electrolysed with a copper anode over the range of current densities possible with the apparatus described and no trace of periodicity was observed. Ammonium acetate, 5 and 2·5%; sodium acetate, 8·4%; acetic acid, 12·4%; ammonium sulphate, 5, 2·5, and 1·25%; sodium nitrate, 5%; sodium hydrogen sulphite, 5 and 1%; potassium iodide, 5 and 1%; potassium chromate, 5 and 1%. With the last two substances, insoluble films immediately formed over the anode.

(2) *Silver Anode.*

Although general considerations would lead one to anticipate that periodic phenomena might be observed at a silver anode in similar circumstances, the practical application is beset with difficulty in consequence of the insolubility of so many silver salts. Only the cyanide experiments can be repeated under precisely analogous conditions, but the insolubility of silver chloride has been overcome by the employment of ammoniacal solutions of chlorides. With these modifications, the phenomena observed are similar to the experiments with a copper anode, but, in general, the effects are much less striking; the amplitude of the oscillations is relatively small and the frequency is in all cases very high. The latter fact precludes direct experiment on the properties of the films, and it is therefore necessary at present to rely on the analogy with copper for an explanation of the phenomena. This seems a safe course in view of the similarity in every respect between the two cases.

Electrolysis of Potassium Cyanide.—Since, except in the strongest

solutions employed, the highest amount of current passing is small, the limits will be defined by the *P.D.* between the electrodes. With a 5% solution, the anode dissolves normally as potassium argentocyanide when the *P.D.* is less than 2·3 volts; at this value, a brownish-black film of silver oxide sweeps up the metal and the potential rises to 3·2 volts and then oscillates rapidly (about twice per second) between 3·2 and 3·0. Simultaneously, the upper part of the anode displays alternate black and white flashes—a rapid periodic dissolution of the silver oxide film by the potassium cyanide. The phenomenon is precisely similar to the case of copper, the black oxide film sweeping up and the white cyanide film rolling down, the frequency increasing with current density, concentration, and temperature. On slightly increasing the current, the alternation is so quick as to resemble a twinkling.

Similar effects were observed in solutions of concentrations 2·5, 1, 0·5, and 0·25%. The 2·5% solution gave an amplitude of 0·4 volt between the critical limits 1·7 and 2·9 volts. Below the value 1·7, no oxide film appeared and above 2·9 it existed permanently. The 1% solution gave an amplitude of 0·4 volt between the limits 1·8 and 2·7 volts. The limiting voltages for the 0·5% solution were 1·8 and 2·4, and in the case of the 0·25% solution they were 1·6 and 1·7. In the last case, the periods were as long as 30 seconds. It is seen from these figures that the extent of the unstable region decreases with progressive dilution.

These results were for unstirred solutions at 20°. In stirred solutions, the frequency was even higher. Since the low amplitude and high frequency of these periods were reminiscent of the anodic dissolution of copper in hydrochloric acid at higher temperatures, some experiments were conducted on silver in potassium cyanide solutions at 0°, and a maximum amplitude of 2·1 volts was then obtained with a 10% solution of potassium cyanide.

Experiments were also conducted in 10 and 5% ammonium thiocyanate solutions. Although above a certain current density the oxide film formed slowly, it seemed to be permanent. The 10% solution was investigated over the temperature range 20—80° in an attempt to quicken the dissolution of the film, but the experiments were not successful in producing periods.

Electrolysis of Ammoniacal Solutions.—When solutions of ammonium chloride were electrolysed with a silver anode, a highly resistant chloride film immediately formed. Attempts were therefore made to add just sufficient ammonia to dissolve the film as fast as it formed. Periodic effects were observed in these experiments, the anode becoming intermittently coated by a dark brown oxide film. The best result was with a solution of 50 c.c. of 10% ammonium

chloride and 50 c.c. of ammonia solution (*d* 0·880). With a current density of 44 milliamp. per sq. cm., the *P.D.* oscillated between 3·0 and 4·1 in periods of 20 seconds. Rapid oscillations were also observed with a silver anode dissolving in a mixture of 50 c.c. of 10% ammonium sulphate solution and 50 c.c. of ammonia (*d* 0·880).

Electrolysis of strong ammonia solutions alone might be anticipated to yield periodic phenomena on the basis of the explanation advanced here. Such solutions were tried without success, but the failure is most likely due to the fact that very little current can be made to pass. Endeavours to obviate this difficulty by adding progressively increasing amounts of caustic soda to the solution met with no success.

Electrolysis of Sulphuric Acid.—Solutions varying in composition from 100 to 2% were electrolysed. The anode dissolved continuously only in the most concentrated solutions, a sulphate film forming above a certain critical current density and the potential rising very sluggishly. Periods were obtained in these systems at higher temperatures. With 90% sulphuric acid at 50°, the waves shown in Graph 55 (Fig. 2) were obtained at a current density of 36 milliamp. per sq. cm., whilst Graph 56 represents 50% sulphuric acid at 75° under a current density of 17 milliamp. per sq. cm. The solutions always became cloudy, preventing observation of the state of the anode.

Electrolysis of Other Solutions.—In addition to those mentioned above, the following solutions gave no periodic effects: caustic soda, 8, 4, and 0·4%; nitric acid, 2, 1, and 0·5%; silver nitrate, 1·7%; acetic acid, 12·4%; potassium chromate, 9·7, 4·8, 2·4, and 0·6%; sodium thiosulphate, 3·4%; sodium hydrogen sulphite, 5%. In the last two cases, where periodicity might have been expected, the reaction followed a complex course, the main product being silver sulphide, whilst the solution developed the smell of hydrogen sulphide.

The investigation is being extended to anodes of other metals and will include the cathodic deposition of metals.

Summary.

Periodic changes in current strength and in the *P.D.* between the electrodes were observed in the anodic dissolution of copper in solutions of hydrochloric acid, ammonium chloride, sodium chloride, cupric chloride, and potassium cyanide, and of silver in solutions of potassium cyanide, sulphuric acid, and ammoniacal ammonium sulphate and ammonium chloride. In every case, periodic film formation over the anode occurred. The case of copper in hydrochloric acid was the subject of a detailed examination. The pheno-

menon took place between certain limiting values of current density and the critical current density required to produce the periods was a linear function of the concentration of the electrolyte. The frequency of the periods increased with rising temperature and concentration, and decreased with rising current density. The periods were not affected by catalytic poisons. At the critical current density, an oxidic film formed over the metal and it was shown that this film was stable above a certain value of the current density; its metastability between this value and the critical current density is believed to be the cause of the phenomenon. This case appears to be typical of all the others investigated.

The author is much indebted to Dr. J. F. Spencer for his interest in these experiments and to the Chemical Society for a grant in aid of the research.

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CXCIX.—*The Existence of the Suboxides of Lead and Thallium.*

By FREDERICK AUFENAST and HENRY TERREY.

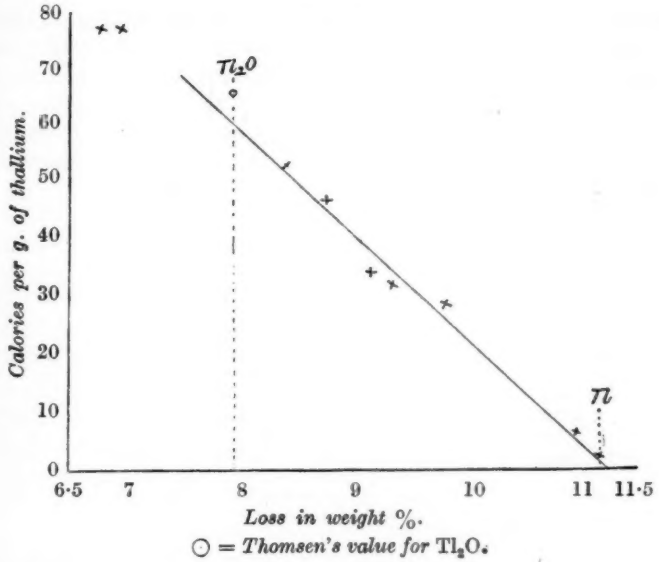
THE black substance obtained by heating lead oxalate has been interpreted as (1) a mixture of litharge and lead, or (2) lead suboxide. The work of Tanatar (*Z. anorg. Chem.*, 1901, **27**, 304) on its heat of reaction with acetic acid pointed to a chemical entity, since he obtained results which indicated a heat of decomposition of lead suboxide into lead and litharge, $Pb_2O \longrightarrow Pb + PbO -$ 5,450 cals. This view is supported by the work of Brislee (J., 1908, **93**, 154) and of Denham (J., 1917, **111**, 29; 1918, **113**, 249; 1919, **115**, 109). Evidence has also been given for the existence of subvalent lead ions by Denham (J., 1908, **93**, 41), Denham and Allmand (*ibid.*, p. 833), and Bell (*Trans. Faraday Soc.*, 1915, **11**, 74).

The similarity of thallium and lead and of many of their salts suggests the possible existence of a thallium suboxide (compare Crookes, *Proc. Roy. Soc.*, 1862, **12**, 150; Lorenz, *Z. anorg. Chem.*, 1896, **12**, 439).

Investigations were first carried out to determine whether breaks could be obtained in the reduction-velocity curves such as were found by Brislee (*loc. cit.*). Thallous oxide was reduced in a stream of hydrogen and the amount of reduction was measured at regular intervals. The results showed in some cases a slight break in the curve corresponding to a compound Tl_4O, but these breaks were

not definite enough to be regarded as satisfactory evidence. Experiments were then made on the heat of solution of the products of varying composition obtained by reduction of thallous oxide, and the results are shown in Fig. 1, in which heats of solution per g. of thallium are plotted as ordinates and the extent to which the thallic oxide had lost weight on reduction as abscissæ. If a suboxide had been present, the heat of solution in 3*N*-sulphuric acid would have included a heat of decomposition of the suboxide and the graph would not have been a straight line. Within the limits of experimental error, no evidence was thus obtained for the existence

FIG. 1.



of thallium suboxide. Attempts were also made to measure the oxidation velocity of metallic thallium, but they were abandoned when it was found that the finely-divided metal was never oxidised completely although the initial velocity was very great.

Similar calorimetric experiments, in which the products of decomposition of lead oxalate were dissolved in acetic acid, gave results indicating that this supposed suboxide was a mixture of litharge and lead.

EXPERIMENTAL.

For the reduction velocity experiments, thallic oxide was precipitated from a thallic chloride solution by ammonia, washed, and heated to 200° in a current of oxygen to remove the last traces

of water. As thallous oxide is very deliquescent, it was decided to measure the reduction by collecting the water evolved rather than by removing the substance and determining the loss in weight. A weighed amount of thallic oxide, spread in a thin layer in a porcelain boat, was gradually heated electrically to 150° in a stream of hydrogen. After a few hours, when scarcely any more water was given off, the temperature was raised to 185° ± 1° and the water produced was collected in calcium chloride tubes which were weighed hourly. The complete reduction to thallous oxide, which took about 30—40 hours, was thus spread over a few days. The product was at first black, changing to a metallic grey colour.

For the heat of solution experiments a known weight of thallic oxide was reduced in a stream of hydrogen to a known composition, and the product was transferred as quickly as possible to the calorimeter, which consisted of a 100 c.c. Dewar vessel fitted with a Beckmann thermometer and a small glass stirrer and containing 25 c.c. of 3*N*-sulphuric acid. The results of these experiments are as follows:

Expt.	Wt. Tl_2O_3 used.	Loss %.	Wt. used for solution.	Rise in temp.	Cals. evolved.	Cals. per g. Tl.
1	0·3926	6·78	0·3657	0·780°	26·86	77·29
2	0·4081	6·96	0·3797	0·809	27·86	77·21
3	0·3669	8·75	0·3242	0·404	13·91	47·36
4	0·4781	8·39	0·4257	0·693	21·44	53·30
5	0·4115	9·14	0·3655	0·400	12·38	34·73
6	0·3494	10·96	0·3029	0·067	2·07	6·81
7	0·3953	11·15	0·3394	0·025	0·77	2·28
8	0·3836	9·33	0·3151	0·325	10·06	32·66
9	0·3693	9·80	0·2848	0·266	8·20	29·51

For Expts. 1—3 and 4—9, the water-equivalent of the calorimeter and its contents was 34·43 g. and 30·94 g. respectively.

These results are shown graphically in Fig. 1, where the figures of column 3 are the abscissæ and those of column 7 the ordinates.

For the preparation of lead suboxide, about 1·5 g. of lead oxalate were heated in a porcelain boat in a vacuum at about 275°; the gas evolved was pumped off periodically, the pressure never being allowed to exceed 1 cm. Evolution of gas ceased after about 24 hours, and the black residue gave off no carbon dioxide when treated with acids. The heat of solution in *N*-acetic acid was determined as with thallium, and after completion of the determination the liquid was filtered from undissolved lead, and the lead in the filtrate and the insoluble lead were determined by conversion into sulphate.

The results of two such experiments are given:

(Water-equivalent of calorimeter and contents = 56·2 g.)

	No. 1.	No. 2.
Weight of suboxide used (g.)	1·332	1·162
Amount of PbO dissolved from suboxide (%)	71·3	68·6
Rise in temperature	1·165°	0·963°
Heat of solution per g.-mol. of PbO (cals.)	15,370	15,140

The mean of these two experiments, *viz.*, 15,250 cals., differs only by about 350 cals. from that obtained with pure litharge, *viz.*, 15,600 cals.

These values are in agreement with those obtained by Sveda (*Chem. Listy*, 1923, **17**, 47, 81, 112), but differ from those of Herschkowitsch (*Z. anorg. Chem.*, 1921, **115**, 159) and Tanatar (*loc. cit.*).

UNIVERSITY COLLEGE, LONDON. [*Received, March 18th*, 1926.]

CC.—*The Precipitation of Cadmium Sulphide from Aqueous Solutions of Cadmium Chloride in the Presence of Hydrochloric Acid and Other Chlorides.*

By SUBRAMONIA KRISHNAMURTI.

THE object of this investigation was to determine the relation between the concentration of cadmium chloride and the minimum concentration of hydrochloric acid required to prevent the precipitation of cadmium sulphide by hydrogen sulphide at constant temperature and pressure, and to ascertain the effect of various chlorides on this relation. It will be seen that the introduction of the activity concept renders this familiar problem of analytical practice capable of much more exact theoretical treatment. The present paper forms an introduction to the study of this and allied reactions from this point of view. Amongst previous workers on the precipitation of sulphides, mention may be made of Bruner and Zawadski (*Bull. Acad. Sci. Cracow*, 1909, 267; *Z. anorg. Chem.*, 1910, **67**, 454), who studied more especially the precipitation of thallous sulphide, and of Baubigny (*Compt. rend.*, 1888, **107**, 1148), who investigated the concentration of free acid required to prevent the precipitation of zinc sulphide from solutions of zinc sulphate. Reference may also be made to the work of Bruni and Padoa (*Atti R. Accad. Lincei*, 1905, **14**, ii, 525) and of Glixelli (*Z. anorg. Chem.*, 1907, **55**, 297).

EXPERIMENTAL.

The apparatus used was very simple. A stream of washed and pre-heated hydrogen sulphide was bubbled through the solution contained in a suitable vessel, placed in a thermostat at 25°. The

gas escaped through an oil-trap. In order to prevent the oxidation of hydrogen sulphide, air-free water was used in making up all solutions, whilst a stream of carbon dioxide was passed through the apparatus and solution for a considerable time before the hydrogen sulphide was admitted. A pre-saturator (also in the thermostat) contained hydrochloric acid of the same concentration as that contained in the precipitation vessel. In order to obtain reproducible results, in addition to the above precautions the precipitation vessel must be cleaned very thoroughly before use. The experiments were carried out by making up a series of solutions having the same concentration of cadmium chloride and gradually increasing concentrations of hydrochloric acid. In this way, two neighbouring solutions were obtained, in one of which a precipitate just appeared whilst in the other it did not. These two solutions were then made the limiting members of a new series in which the acid concentrations were graded more closely than before, and the interval between precipitation and non-precipitation was thus more accurately determined. Proceeding in this way, it was found possible to distinguish between two solutions differing by not more than 0·1*N*. The mean of these two hydrochloric acid concentrations was taken as giving the "critical" concentration for the given solution of cadmium chloride (expressed as mols. per litre), and the results are in the first two columns of Table I.

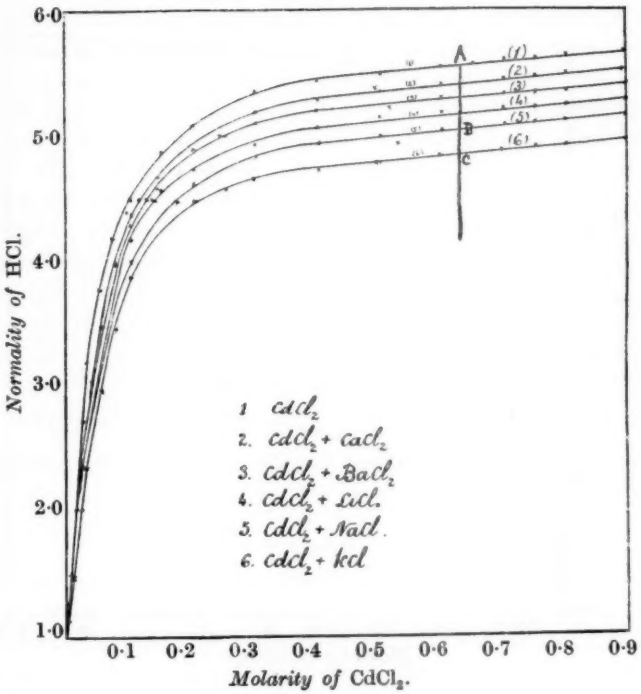
A second series of experiments was made with solutions in which the chloride of potassium, sodium, lithium, barium, or calcium was added so as to be present in *N*-concentration. The results are in the last five columns of Table I, which show in each case the critical concentrations of hydrochloric acid corresponding to each concentration of cadmium chloride.

TABLE I.

	Limiting concentrations of HCl in the presence of					
$CdCl_2$.	—	*N*-KCl.	*N*-NaCl.	*N*-LiCl.	*N*-$BaCl_2$.	*N*-$CaCl_2$.
0·005	1·50	1·20	1·30	1·35	1·40	1·40
0·01	2·05	1·50	1·60	1·65	1·75	1·80
0·03	3·20	2·40	2·50	2·55	2·60	2·65
0·05	3·80	3·00	3·15	3·25	3·35	3·50
0·08	—	3·50	3·60	3·75	4·10	4·15
0·10	4·50	3·90	4·00	4·20	4·30	4·40
0·20	5·20	4·50	4·60	4·70	4·90	5·00
0·30	5·40	4·60	4·85	4·95	5·10	5·20
0·40	5·45	4·75	4·95	5·05	5·20	5·30
0·50	5·55	4·80	5·00	5·15	5·25	5·35
0·60	5·60	4·85	5·05	5·20	5·30	5·40
0·70	5·65	4·90	5·10	5·25	5·35	5·45
0·80	5·70	4·95	5·10	5·25	5·35	5·50
0·90	5·70	4·95	5·15	5·30	5·40	5·55
1·00	5·75	5·00	5·20	5·30	5·40	5·60

The results contained in Table I are shown in Fig. 1. It will be seen that the critical concentration of hydrochloric acid increases very rapidly with increase of cadmium chloride concentration for the lower concentrations, whilst for the higher concentrations the variation of the hydrochloric acid concentration is comparatively small. It will also be seen that the effect of the neutral chlorides is to lower the critical concentration of hydrochloric acid corresponding to any given concentration of cadmium chloride, which

FIG. 1.

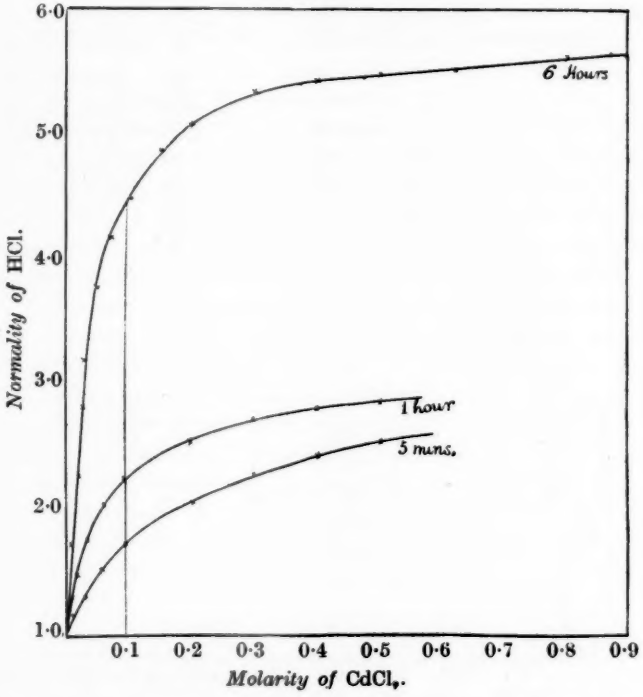


means that in the presence of these chlorides a lower concentration of hydrochloric acid suffices to prevent precipitation of cadmium sulphide, thus pointing to an activation of the acid by the neutral chloride.

The Time Factor.—A surprising feature of these results is the relatively high concentrations of hydrochloric acid required just to prevent precipitation. This critical concentration increases rapidly with time. Passing in hydrogen sulphide for 5 minutes and for 1 hour, respectively, gave the results shown in the two lower curves of Fig. 2. On increasing the duration of passage of the gas, the

critical concentration of hydrochloric acid steadily rose, reaching a limit after about 6 hours (see highest curve), *i.e.*, further passage of the gas produced no measurable variation in the required concentration of acid. Glixelli (*loc. cit.*) noticed a similar "period of induction" in his experiments on the precipitation of zinc sulphide. The experimental results given in Table I correspond in all cases to a duration of 6 hours for the passage of hydrogen sulphide. The

FIG. 2.



influence of this apparent supersaturation effect is shown in Table II, which gives, for a 0·1*M*-solution of cadmium chloride at 25°, the critical concentrations of hydrochloric acid corresponding to different lengths of time.

TABLE II.

Mols. HCl per litre	1·7	2·3	4·5
Time (min.)	5	60	300

E.M.F. Measurements.—If we apply the simple laws of chemical equilibrium to the ionic reactions occurring in such a precipitation of sulphide, then, for the points on the "precipitation curve"

(*i.e.*, the curve separating the region of precipitation from that of non-precipitation), we have the two equations

$$[Cd^{\cdot\cdot}] \,.\, [S''] = const.$$
$$[H^{\cdot}]^2 \,.\, [S''] = K[H_2S].$$

The first equation involves, of course, the doubtful assumption that the points on the precipitation curve correspond to equilibrium with a definite crystalline cadmium sulphide present in not too fine a state of division. If we assume further that the solubility of the hydrogen sulphide and also its dissociation constant do not appreciably change with the total electrolyte content of the solution, then the right-hand member of the second equation remains constant, and division of the equations gives $[Cd^{\cdot\cdot}]/[H^{\cdot}]^2 = const.$, an equation which is often used in elementary treatises on the theory of inorganic analysis. For very dilute solutions, we may use the approximate form $[CdCl_2]/[HCl]^2 = const.$ If we apply this equation to the results given in columns 1 and 2 of Table I for the dilute solutions of cadmium chloride (although the corresponding concentrations of hydrochloric acid are by no means dilute), we obtain the results shown in Table III : the quotient rises slowly.

TABLE III.

$[CdCl_2]$	0·005	0·01	0·02	0·03	0·05	0·10
$[HCl]$	1·50	2·05	2·75	3·20	3·80	4·50
$10^4 \times [CdCl_2]/[HCl]^2$ ...	22	25	26	29	34	49

Rewriting the former equations in terms of activities, we have

$$a_{Cd} \,.\, a_S = L$$
$$a_H{}^2 \,.\, a_S = K_1 a_{H_2S}$$

where L is the activity of the solid sulphide and K_1 the " thermodynamic " dissociation constant of hydrogen sulphide. Since the temperature and the pressure of hydrogen sulphide in the gas phase are constant, a_{H_2S} is now strictly constant. We may also regard K_1 as a constant, hence for points on the precipitation curve

$$a_H{}^2/a_{Cd} = K_1 a_{H_2S}/L = const. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation will be much more exact than the former one, although it still involves the assumption that we are dealing, along the precipitation curve, with a definite " solid " cadmium sulphide of not too small a grain size, or, at all events, of constant grain size in the different experiments. It is possible to test equation (1) by measuring the *E.M.F.* of cells of the type Cd amalgam | $CdCl_2$+HCl | H_2 gas at constant pressure. A dilute cadmium amalgam of definite concentration is used instead of solid metallic cadmium, in order to

avoid irreversible evolution of hydrogen at the cadmium electrode. The *E.M.F.* of the cell is given by the equation

$$E = E_0 + RT/2F \cdot \log a_H^2/a_{Cd} \quad . \quad . \quad . \quad . \quad (2)$$

Hence, if we employ in the cell solutions corresponding in composition and concentration to points on the precipitation curve, E will be constant if equation (1) holds good for such points, since we may neglect the effect of the dissolved hydrogen sulphide. Cells of this sort were set up, with hydrogen electrodes of the usual type, and yielded constant and reproducible results after an hour. The results are in Table IV (to the nearest millivolt).

TABLE IV.

$CdCl_2$ (mol./litre)	0·005	0·01	0·02	0·05	0·08	0·10	0·20	0·30	0·50
HCl (mols./litre)	1·50	2·05	2·75	3·80	4·20	4·50	5·20	5·40	5·55
E.M.F. (millivolts)	481	481	481	481	482	481	482	482	480

The constancy in the *E.M.F.* indicates that the points on the observed precipitation curve do correspond to definite equilibria, and supports the view that this curve is a true border curve separating the region of precipitation from that of solution (non-precipitation).

Neutral Salt Effect.—The curves numbered (2) to (6) in Fig. 1 show the changes in the precipitation curve caused by the presence (in N-concentration) of a series of neutral chlorides. The interpretation of these neutral salt effects from the point of view of ionic activities can be seen from a consideration of the figure. At the point A on the precipitation curve of cadmium chloride (*i.e.*, without addition of any neutral chloride) we have the relation

$$a_H^2/a_{Cd} = K_1 a_{H_2S}/L.$$

Suppose now that the solution corresponding to point A is made N with respect to, *e.g.*, potassium chloride, everything else remaining the same. Since A lies above C, it is clear that A now falls in the non-precipitation region, and hence $a_{Cd} \cdot a_S < L$. In the mixed solution corresponding to point A, therefore, $a_H^2/a_{Cd} > K_1 a_{H_2S}/L$. The effect of the addition of potassium chloride has thus been to increase the value of the quotient a_H^2/a_{Cd} and this value can be brought back to the original value, $K_1 a_{H_2S}/L$, only by reducing the concentration of hydrochloric acid to the value corresponding to point C. Now it is well known that the addition of chlorides can increase the value of a_H in a solution of hydrochloric acid (Poma, *Z. physikal. Chem.*, 1914, **88**, 671; Harned, *J. Amer. Chem. Soc.*, 1915, **37**, 2460; Fales and Nelson, *ibid.*, 1915, **37**, 2769; Thomas and Baldwin, *ibid.*, 1919, **41**, 1981). In the present case, this action will produce

a very marked result, owing to the occurrence of a_H^2 in the numerator of the quotient. It is probable that owing to complex anion formation and other causes the addition of chlorine ions (from the neutral chlorides) will *decrease* the value of a_{Cd} occurring in the denominator. We have therefore good reasons for concluding that the addition of a neutral chloride will increase the value of a_H^2/a_{Cd}.

If we ascribe the chief effect to the increase in the value of a_H, we should expect from the results of the investigations previously quoted that the effect would decrease in the order LiCl > NaCl > KCl, whereas the results in Table I would appear to give the order KCl > NaCl > LiCl.

Further discussion of this matter would not be profitable without more detailed and extensive data.

Summary.

1. The concentrations of hydrochloric acid which are just sufficient to prevent precipitation of solutions of cadmium chloride by hydrogen sulphide at 25° and atmospheric pressure have been determined.

2. The effects produced on these critical concentrations of hydrochloric acid by a number of neutral chlorides in *N*-concentration have been determined.

3. The cadmium chloride–hydrochloric acid "precipitation" curve has been considered from the point of view of ionic activity, and predictions based thereon have been confirmed by *E.M.F.* measurements.

4. The effects produced by the addition of neutral chlorides have been considered in the light of previous work on the influence of such salts on the hydrogen-ion activity.

5. The precipitation experiments reveal a "supersaturation" or "induction" delay in the appearance of the precipitate, an effect previously noted by Glixelli in the precipitation of zinc sulphide.

It is intended to extend this investigation and to include allied cases.

The work described was carried out at the suggestion and under the direction of Professor F. G. Donnan, to whom the author desires to express his thanks for advice and assistance.

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CCI.—*The Interaction of Hydrogen and Nitrous Oxide on the Surface of Gold.*

By WILLIAM KENNETH HUTCHISON and CYRIL NORMAN HINSHELWOOD.

IN catalytic reactions at surfaces considerable variety is found in the relations which exist between the rate of reaction and the concentrations of the several reacting substances. Examples of different kinds have been given in a number of previous papers. The most general relation, when there is one reacting substance only, is that the rate increases with concentration according to a curve of the same form as an adsorption isotherm. When there are two reacting substances, the rate may actually pass through a maximum and decrease again as the pressure of one gas increases, the decrease being due to the displacement of the other gas from the surface. But it may happen that the two reacting substances are independently adsorbed on different active parts of the surface. Saturation can then be reached with respect to each gas without displacement of the other. Examples of these two kinds of behaviour are given in J., 1925, **127**, 806, 1546. For the sake of completeness in classifying the various types of heterogeneous reaction, further instances may be useful.

We have now investigated the kinetics of the interaction of hydrogen and nitrous oxide on the surface of a gold wire. The results can be interpreted by assuming that hydrogen and nitrous oxide are adsorbed on the surface independently of each other, and that interaction can take place between adjacent molecules. The reaction rate increases with increase in the pressure of nitrous oxide, and reaches a limiting value at approximately 300 mm., after which it remains constant up to the highest pressure used, *viz.*, 500 mm. The absence of any fall in the rate at the higher pressures may be taken to show that, even after saturation is reached, there is no appreciable tendency for the nitrous oxide to displace the hydrogen from the surface.

Increase of hydrogen pressure has a similar effect, except that the limiting value of the rate is not quite reached within the experimental limit of 500 mm.

A second effect was traced to the hydrogen, namely a steady decrease in the activity of the wire, especially when it was heated in mixtures containing hydrogen in excess. On a wire, the activity of which had been reduced in this way to less than one-fifth of its initial value, it was found that the influence of the nitrous oxide on the rate was more nearly proportional to its pressure, and that the

limiting or saturation value could not be reached. It is suggested that hydrogen gradually dissolves in the body of the metal—this solution being distinct from its primary adsorption on the surface—and decreases the adsorptive power towards nitrous oxide. This would result, not only in a decrease in the rate of reaction due to the smaller number of nitrous oxide molecules present on the surface, but also in a change in the actual adsorption isotherm.

The method of procedure was that already described (*loc. cit.*), the change in pressure giving a measure of the reaction

$$N_2O + H_2 = N_2 + H_2O \text{ (liquid)}.$$

A correction was necessary for the vapour pressure of liquid water at 0° in those cases where no drying agent was present. The experimental work was complicated by the continually decreasing activity of the catalyst. Heating to dull redness in air caused a partial but only temporary recovery, for it rendered the wire very susceptible to the further action of hydrogen. The following method was therefore employed to correct for the variable activity, and to reduce the results to values which are comparable with one another. Initial rates of reaction only were observed, and in any series, the first, third, and odd-numbered experiments were performed under standard conditions of concentration of the reactants (for convenience, 100 mm. of each), and in the even-numbered experiments the initial pressure of one or other reactant was varied. The ratio of the observed initial rate in an even-numbered experiment to the mean value of the rates observed in the reference experiments on either side of it gives a value which is strictly comparable with the others in a given series, even if the state of activity of the catalyst drifts to some extent.

Owing to this gradual poisoning of the catalyst, and also on account of the complicated relation which would be required to express the velocity in terms of the concentration of both reactants, no attempt was made to evaluate velocity coefficients, nor to determine the heat of activation. The experiments were carried out in the usual manner at two temperatures with a number of different wires, and in the tables which follow it will be seen how the initial rate of reaction depends upon the initial pressure of nitrous oxide and of hydrogen. If, as seems probable, the rate is determined by the amount of adsorption or surface concentration, these figures represent also the relative degrees of saturation of the active parts of the surface with the gas in question.

Influence of Nitrous Oxide.—On a fresh active wire the initial rate reaches a limit at a pressure near 300 mm. and remains constant up to a pressure of at least 500 mm.

TABLE I.

Pressure of hydrogen = 100 mm.

	Pressure of N_2O (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1·00	1·40	1·64	1·91	1·80	Wire 1	704°
„ „ ...	1·00	1·18	1·34	1·37	1·38	Wire 2	704°
„ „ ...	1·00	—	1·25	—	1·26	Wire 3	704°
„ „ ...	1·00	—	1·77	—	1·89	„	880°

With a wire in a highly poisoned and inactive state, as a result of the prolonged action of hydrogen, saturation was not reached, and the rate varied considerably more extensively with the initial pressure of nitrous oxide.

TABLE II.

Pressure of hydrogen = 100 mm. (Wire poisoned.)

	Pressure of N_2O (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1·00	1·50	2·10	2·50	—	Wire 2	704°
„ „ ...	1·00	1·76	2·56	3·13	3·68	„	880°

Influence of Hydrogen.—The influence of the pressure of hydrogen on the rate appears to be independent of the state of the wire, as the figures of Table III show. Saturation is not reached so readily as in the case of nitrous oxide.

TABLE III.

Pressure of nitrous oxide = 100 mm.

	Pressure of H_2 (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1·00	1·33	1·58	1·97	2·22	Wire 4	704°
„ „ ...	1·00	1·21	1·50	1·78	1·92	Wire 4	704°
„ „ ...	1·00	1·18	1·43	1·40	1·81	Wire 2 (poisoned)	880°

Influence of Water Vapour.—Experiments were performed in which phosphoric oxide was present either in the bulb or in a small side tube sealed to it. The rate was reduced somewhat, as compared with that observed on the same wire before the introduction of the phosphoric oxide, and a certain recovery took place when the side tube containing it was sealed off, but the change was not fundamentally important. Further, a comparison of the results contained in Tables IV and V with those already discussed shows that the adsorption isotherms remain of the same form, whether water vapour is present or not.

This reaction possesses some interest in connexion with the general classification of heterogeneous reactions, as it represents

TABLE IV.

Pressure of hydrogen = 100 mm. (Fresh wire.)

	Pressure of N_2O (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1·00	1·34	1·56	1·59	(1·31)	Wire 5	704°

TABLE V.

Pressure of nitrous oxide = 100 mm. (Fresh wire.)

	Pressure of H_2 (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1·00	1·63	—	2·00	2·73	Wire 5	704°

one of the most general cases. But rather will it be in certain special circumstances, for example, with very small or very large adsorption of one reactant, that further theoretical inferences will become possible.

Summary.

The relation between the rate of interaction of nitrous oxide and hydrogen at the surface of a gold wire and the concentrations of the two gases has been examined at 704° and 880°. The reaction is of the type where the two gases are adsorbed independently of each other. The rate of reaction tends to a limiting value as the pressure of each gas is increased.

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CCII.—*The Specific Heats of Hydrogen Cyanide. A Reply.*

By JAMES RIDDICK PARTINGTON.

A RECENT statement [(Mrs.) Ingold, this vol., p. 26] that there is no "obvious disagreement between the author's results and those of Partington and Carroll" for the ratio of the specific heats of hydrogen cyanide seems to call for correction. Whereas the value found by the last two experimenters at 20° was 1·282 (422 mm.), that of Mrs. Ingold at the lowest temperature used, 65°, was 1·310 (1 atm.), and the curve in Fig. 2 in Mrs. Ingold's former paper (J., 1922, **121**, 1610) would indicate that at 20° the value should be of the order of 1·315, which is 2·3% higher than the value found by Partington and Carroll (*Phil. Mag.*, 1925, **49**, 665). It is not considered that such agreement is satisfactory.

Mrs. Ingold has discussed in a very general manner the statement that " although the vapour is associated, the association is small " (Partington and Carroll, *ibid.*, p. 680). Since the critical data were not known at the time, the latter authors contented themselves with an approximate calculation, but the statement that this was " unjustified " is not confirmed by an examination of the paper. Some caution is necessary in approximate calculations, but this must not be mistaken for doubt as to the approximate validity of the results found. In reality, as Mrs. Ingold points out, the calculation of the critical constants has been very satisfactorily confirmed by the experiments of Bredig and Teichmann (*Z. Elektrochem.*, 1925, **31**, 449), which appeared later, and these authors have repeated our calculations of c_p/c_v from our own and Mrs. Ingold's experiments and have shown that they are very close to those obtained with the actual experimental data for the critical constants. The regular nature of the curve in Fig. 2 in Mrs. Ingold's first paper would therefore seem to be disturbed in the manner previously pointed out by Partington and Carroll.

It would seem possible to test the assumption of a small association of hydrogen cyanide vapour by a calculation of the density on the assumption that deviations from the gas laws alone, without association, are operative, and then comparing the results with the experimental values. The method used is one which, it is stated (Ingold, this vol., p. 26), has " proved conclusively that, despite its enhanced density, the degree of association of water vapour, if not zero, is at any rate so small that the most accurate available measurements fail to show it." The densities have been calculated from the ideal value by division by

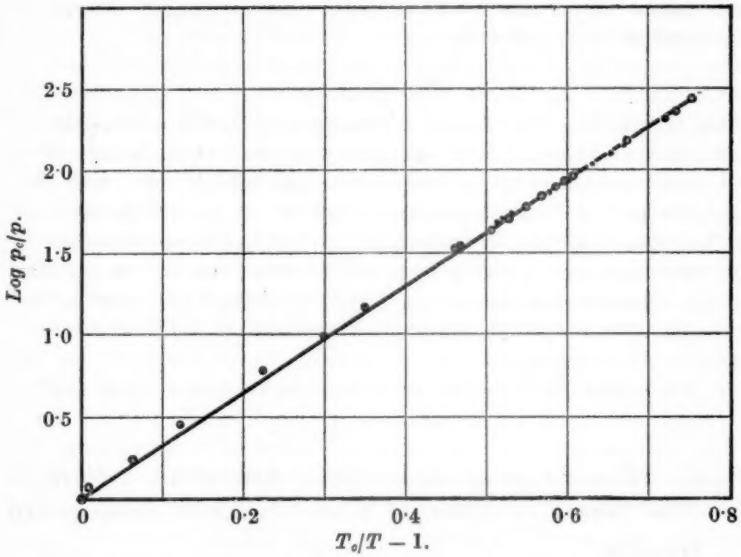
$$\lambda = 1 + \frac{9}{128}\pi\tau(1—6\tau^2)$$

in accordance with Berthelot's equation, which may be expected to apply with some accuracy at atmospheric pressure. In this expression, π and τ have been calculated from the critical data of Bredig and Teichmann ($p_c = 53{\cdot}2$ atm.; $T_c = 456{\cdot}6°$). The results in Table I indicate that, below 100°, the calculated densities are distinctly lower than those found by Mrs. Ingold. At 65°, the observed density, which lies on the smooth curve, is 2% higher than that corrected for deviations from the gas laws, although the experimental error is stated to be only 0·2%. (The two observed values at 132° and 175° lie well below the smooth curve.) This seems to indicate that, if the density measurements are as accurate as they are claimed to be, there must be some such small association of hydrogen cyanide vapour as was assumed by Partington and

Carroll, and that the opposite conclusion, arrived at by Mrs. Ingold on very general grounds, and without specific reference to hydrogen cyanide, is improbable.

In a cursory reference to Bredig and Teichmann's paper, Mrs. Ingold has not emphasised the fact that these authors show, by no fewer than five different sets of experimental data, that hydrogen cyanide is associated in the liquid state and that they express agreement with our calculations for the gas.

FIG. 1.



It is also of interest to plot the values of $\log p/p_c$ against those of $(T_c/T - 1)$, in the manner used by van der Waals. Bredig and Teichmann refer to this in their paper, but do not reproduce the

TABLE I.

$t°$ C.	$T°$ abs.	τ.	λ.	Δ obs. (air = 1).	Δ obs. (O = 16).	Δ calc.
65	338·1	1·3505	0·9822	0·968	14·06	13·77
96	369·1	1·2371	0·9866	0·951	13·79	13·70
97·5	370·6	1·2321	0·9868	0·952	13·80	13·70
132	405·1	1·1271	0·9901	0·936	13·57	13·66
140	413·1	1·1053	0·9907	0·938	13·60	13·65
175	448·1	1·0190	0·9930	0·932	13·51	13·61
177	450·1	1·0145	0·9931	0·934	13·54	13·61

curve. This curve has been constructed from the data of Bredig and Teichmann (*loc. cit.*) and of Perry and Porter (*J. Amer. Chem. Soc.*, 1926, **48**, 299), the former being denoted by circles and the latter by dots on the curve. It will be seen from Fig. 1 that practi-

cally all the points lie on a straight line passing through the origin. The gradient of this line is 3·26. According to van der Waals the normal value is 3·0, whilst from the curve for water given by Nernst ("Theoretische Chemie," 8—10 Aufl., p. 248) the value 3·3 is found. It may be remarked that, in reality, the gradient depends somewhat on the molecular weight and that, although it is reasonable to compare water and hydrogen cyanide as associated substances, carbon disulphide, for which the gradient is lower than 3, should probably be chosen as a normal substance for comparison. There would seem to be very little, if any, doubt that hydrogen cyanide is associated in the liquid state.

Summary.

It is shown that the reasons advanced against the assumption of Partington and Carroll that hydrogen cyanide vapour is associated to a small extent at room temperature are inconclusive, and that when the qualitative arguments put forward on general grounds are applied quantitatively to the specific case of hydrogen cyanide they lead to conclusions exactly opposite to those arrived at by Mrs. Ingold. Attention is also drawn to the fact that all the experimental evidence, of various kinds, points to association in the liquid state.

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CCIII.—*The Laws of Aromatic Substitution. Part V. The Directing Effect of Electrolytically Dissociated Groups.**

By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES.

IN previous communications of this series (*J. pr. Chem.*, 1902, **66**, 321; 1905, **71**, 497; 1907, **76**, 165, 185) it was shown, *inter alia*, that the position in which a second substituent will enter a mono-substituted benzene ring (whether *op*-, or *m*-) can be unequivocally predicted from the affinity demand of the first substituent. In subsequent papers, a more general theory of reactivity was evolved, in which, beside the *affinity demand* (the "quantitative factor" = q), the varying *nature of the affinity* of atoms ("polar factor" = p) and their *steric effects* ("steric factor" = s) were taken into consideration. A review of the whole subject has recently been published in *Chemistry and Industry* (1925, **44**, 246).

* A brief preliminary communication of the ideas and the scope of the experiments contained in this paper is to be found in *Chem. and Ind.*, 1926, **45**, 43.

Whereas generally account must be taken of all three factors, there are cases, and even classes, of reactions where one or even two of them can be neglected. Thus the steric hindrance exercised by a first substituent in benzene affects substitution in the *o*-position, but its effect, and still more the difference of its effects, in the *m*- and *p*-positions are negligible. On the other hand, the polar effect of most substituents cannot be neglected in *any* position, but even here the *difference* of their influence on the *m*- and *p*- carbon atoms could be ignored in all the cases hitherto examined. This has been definitely established by numerous observations; thus, not even an accumulation of "negative" groups such as obtains in bromocyanophenylnitromethane, $C_6H_5 \cdot CBr(CN) \cdot NO_2$, can prevent the essentially exclusive *op*-substitution predicted from the affinity demand of the substituent (compare *J. pr. Chem.*, 1902, **66**, 321).

In view of this, an observation by Noelting and Kregczy (*Bull. Soc. chim.*, 1916, **19**, 355) seemed at first sight surprising. These authors nitrated diethylbenzylamine in sulphuric acid solution and obtained 35 to 40% of the *m*-nitro-derivative. Since the affinity demand of the substituent should lead to *op*-nitration only, this experiment has now been repeated, and through the use of very accurate methods of separation the yield of the *m*-nitro-compound has been found to be even higher, *viz.*, 44% of the isomerides formed.

This result could not be ascribed to nitration of the *free base*, since the hydrolysis of such a relatively strong base in an excess of strong sulphuric acid would be negligible. Neither could it be due to nitration of the *salt*, which should occur only in the *o*- and *p*-positions. Reference to the work of Walden and others having shown that salts possess a high degree of electrolytic dissociation in strong sulphuric acid, even at high concentrations, the question whether *m*-nitration of the *electrolytic ion* would be in accordance with the theory was next considered. Concerning the relative polar effects of different atoms, it had already been pointed out (J., 1909, **95**, 719) that an electric charge may be regarded as the most polar element. The meaning of this statement may be briefly explained.

Discarding all speculations concerning the origin and nature of chemical affinity, what we really *know* about it appears to be this: 1. Chemical affinity, like gravitational and magnetic forces, is *some* function of an atom. 2. Although atoms contain positive and negative electrical charges, there is no compelling reason for assuming that chemical force, any more than gravitational or magnetic force, is electrostatic. 3. The behaviour of atoms, not only towards electrical charges, but also *towards one another*, proves that chemical affinity varies in different atoms both in *amount* and in *kind*. The difference in kind is most pronounced between the

atoms of the elements situated at the opposite ends of a period in the periodic table and *gradually* diminishes with the number of intervening members of the period. The more two atoms differ as to the kind of their affinity, the greater is the difference in their tendencies to combine, either with a third atom located towards either end of a period, or with an electrical charge of a given sign.

We may conclude that the variation in kind exhibited by chemical affinity implies a *gradual transition in polarity*, involving a change of sign at a given point in a period. *This gradual transition, if extended far beyond the terminal members of a period, would lead to polarity in its extreme form—electropolarity.* In other words, *whilst electropolarity exists only in two extreme kinds of opposite sign, chemical polarity, gradually varying in kind, bridges a limited central region in the wide gap between the two electropolar extremes.* Thus, in view of the strong affinity of fluorine for an electron as well as for lithium, the corresponding period might be written:

$$\ominus \;.\;.\;.\;.\;.\;.\;.\; \overset{-}{\longleftarrow} \text{Li,Be,B,C,N,O,F} \overset{+}{\longrightarrow} \;.\;.\;.\;.\;.\;.\;.\; \oplus,$$

polar attraction between two members of opposite sign, and polar repulsion * between a given member and a more polar one of the same sign, running parallel with their distance apart within the period. This is what is meant by the polar factor p or "polar effect," or, to use the term recently introduced by Lapworth, by "general polarity."

The polar attraction by a negative charge, and the polar repulsion by a positive charge, of a halogen atom, nitro-group, etc., therefore considerably exceed the corresponding effects of an electrically neutral atom or group on these atoms or groups. Accordingly, since the polarity of such a charge is transmitted to different nuclear carbon atoms in different degrees ascertainable from the theory itself (J., 1910, **97**, 85), a positive charge tends to direct an entering nitro-group, etc., to the least affected nuclear carbon atom, whereas a negative charge tends to direct it to the most affected carbon atom. In the benzoic anion and the diethylbenzylammonium kation, for instance, the nuclear atoms are affected in the order $o->p->m-$ (on account of the direct neutralisation of residual affinity between the p-atoms which results in the *direct* transmission of the polar effect from the substituted atom to the p-atom) (see *loc. cit.*), so that the overpowering p of the electrical charge must favour substitution in the order $o->p->m-$ in the benzoic anion and $m->p->o-$ in the diethylbenzylammonium kation. Besides, it must have an acceler-

* "Repulsion" is used in a relative sense only, to denote a reduced potential at corresponding points in the field of mutual attraction of the atoms. The affinity of neon, whilst much smaller in amount than that of fluorine, must be even more polar in kind.

ating effect in the anion and a retarding effect in the kation, as compared with the corresponding neutral compound.*

This is exactly what has been found to occur. Electrolytically dissociated sodium benzoate is chlorinated by hypochlorous acid (Lossen, D.R.-P. 146, 174) with remarkable ease and in the order *o*–>*p*–>*m*–, whereas benzoic acid itself is brominated, by hypobromous acid, slowly and in the meta-position (Stark, *Ber.*, 1910, **43**, 473). Electrolytically dissociated benzyldiethylammonium hydrogen sulphate is nitrated in the meta-position and more slowly than the undissociated salt, since *m*-substitution in an approximately normal solution amounts to 44% only, although the degree of dissociation of binary salts in strong sulphuric acid at a corresponding concentration is of the order of 80 or 90%.

The theoretical support thus afforded for the assumption that the observed *meta*-nitration is due to the electrolytic ion has been supplemented by direct experimental proof. The assumption requires that increased electrolytic dissociation should lead to increased *meta*-substitution, and *vice versa*. This has been found to be the case. At double the dilution, 52% of the *m*-nitro-derivative was formed, the increase being in approximate agreement with the value calculated from the increase in dissociation required by Sugden's cubic root law on the basis of *exclusive m*-nitration of the ion and exclusive *op*-nitration of the undissociated salt (see experimental part); any appreciable *op*-substitution in the ion and/or *m*-substitution in the salt would, according to Sugden's law and still more according to other dilution laws, have caused the increase in the amount of *m*-nitration to be correspondingly below the experimental result. Similarly, the introduction of a common ion by saturation of the nitrating solution with ammonium sulphate resulted in lowering the amount of *meta*-compound formed to 34%. In this case, only an approximate calculation is feasible, but it shows the decrease to be of the right order. If the dissociation of the sulphuric acid solvent itself (to which Dr. Sugden has kindly called the authors' attention) produced a common ion, then the change in *m*-nitration with varying concentration would be even greater than required by Sugden's law.

Complications such as have now been dealt with, where the uniquely strong *p* of an electrical charge conflicts with and outweighs *q*, can occur only where the charge is carried by an atom separated from the nucleus by *one* intervening atom. When the charged

* This effect of the polar factor on the *velocity* of aromatic substitution has repeatedly been emphasised by one of the authors (*e.g.*, *Ber.*, 1906, **39**, 2016; *J. pr. Chem.*, 1907, **76**, 200), and its electronic equivalent recently by Robinson (this vol., p. 410) and co-workers.

atom is directly attached to the nucleus, *p* and *q* support each other. When the charged atom and the nucleus are separated by two or more atoms, the polar factor even of an electrical charge may be presumed to become negligible, at least as regards its effect on *m*- versus *p*-substitution.

The present results appear to supply a conclusive solution of the problem of *m*-nitration in solutions of benzylammonium salts and to be in complete agreement with the theory advanced by one of the authors. Apart from this they seem to show, for the first time, a way in which the changes of the "degree of dissociation" can be ascertained without interference from disturbing factors such as variations in viscosity, ionic mobility, and solvation. The results also furnish, perhaps not a final proof, but at least a strong argument against the theory of the complete dissociation of strong electrolytes and of the intramolecular ionisation of undissociated ammonium salts. On these views, the undissociated salt in solution would have to be replaced by its two ions in more or less close proximity. But in this case, the charge on the kation would be substantially nearer to the benzene ring than would the charge on the anion, and though it is perhaps not entirely impossible, it is at least highly improbable that the latter charge could seriously interfere with the transmission to the ring of the pronounced polar effect of the first charge. What appears quite certain, however, is that it could not do so in the case of Robinson's mechanism of transmission. Robinson, who has adopted the electronists' view that an ammonium group is ionised even in the undissociated salt (J., 1922, **121**, 430), attributes *meta*-substitution to a "Lewis" electron shift towards the ammonium group caused by its positive charge (*Chem. and Ind.*, 1925, **44**, 563; this vol., p. 410). But such a shift would occur both in the electrolytically dissociated and in the undissociated state, since in the latter the attraction of the electron by the positive charge would, according to Coulomb's law, be compensated by the repulsion of the more distant anionic charge only to a fractional extent (less than one-quarter). It would be less compensated than a positive charge on carbon in carboxyl, carbonyl, trichloromethyl, or on nitrogen in a nitro-group (since the acid radical is generally recognised to be at a greater distance from ammonium nitrogen than oxygen is from carbon or nitrogen, or than chlorine is from carbon), all these being cases where Robinson (*loc. cit.*) attributes *meta*-substitution to such a positive charge, thus obviously assuming it to be insufficiently compensated. Contrary to the experimental results, Robinson's theory would therefore require *meta*-substitution in the undissociated as well as in the dissociated portion, especially since his alternative (conjugation) cannot be applied in this case.

Neglect of the polar and steric factors in classes of reactions where —as has repeatedly been emphasised—they must not be neglected, has recently led several authors to erroneous objections, which will be dealt with in a subsequent communication.

Experimental.

Three series of nitrations of diethylbenzylamine were carried out. The first of these served to establish the best method of separating the isomerides formed. The second series (nitrations 1 to 5 in the table) gave the approximate results obtained by that method, whereas in the final series (nitrations 7 to 10) quantitative values were obtained by the determination of that portion of the *m*-nitro-compound which could not be separated as such.

The nitrations were carried out by Noelting and Kregczy's method (*loc. cit.*), but at $-10°$ to $0°$ instead of $-5°$ to $+5°$. Nitric acid (Kahlbaum, "*d* 1·52") was used, except in No. 5, where ordinary fuming nitric acid served both as nitrating agent and as solvent. In Nos. 8 and 10, the nitrated mixture was kept at room temperature for 1½ hours, and 4 hours, respectively, instead of the usual 1 hour. To prevent any volatilisation of the nitro-bases formed, the benzene extract containing them was treated with picric acid before evaporation to dryness. The yield of crude nitro-bases was always close to 97·0% of the theoretical, and the picric acid added (2·60, 4·0, 6·71, 7·10, 2·60, 3·417, 6·48, 4·286, and 4·480 g., respectively, in nitrations 1 to 5 and 7 to 10) was either 97% of the theoretical or slightly more. The freezing-point method being untrustworthy in the presence of even small amounts of impurities, and fractional distillation of the free bases having failed, there only remained the following method, involving the use of an analytical balance throughout and weeks of work for each nitration of the final series :

The bulk of the relatively insoluble picrate of the *m*-isomeride was obtained pure by prolonged fractional recrystallisation from alcohol (see Noelting and Kregczy); this was preferably preceded by fractional extraction with small amounts of the solvent. This fractionation was carried especially far in Nos. 1, 8, and 10. In Nos. 2, 3, and 5, the pure picrate of the *p*-nitro-compound was also isolated, by further recrystallisation from glacial acetic acid, to the extent of 1·60, 2·30, and 1·09 g., respectively. The purity of the picrate of the *m*-nitro-compound was established by its correct and constant melting point, by the melting point of a mixture with a sample prepared from *m*-nitrobenzyl chloride and diethylamine, and by its oxidation to *m*-nitrobenzoic acid. The purity of the picrate of the *p*-compound, where isolated, was established by its correct

and constant melting point, and by the melting point of a mixture with synthetic material. The pure picrate, m. p. 122°, of the *o*-nitro-compound could only be obtained synthetically (Noelting and Kregczy give 117°). The *picrate* of diethylbenzylamine itself crystallises in stout, yellow prisms, m. p. 120°. In the final series, the picrate of the *m*-nitro-compound left behind in the *op*-mixture was thus determined : 1 part of the picrate mixture was boiled under reflux with 120 parts of water and 2 parts of potassium permanganate. At intervals of 30 minutes three further additions of 2 parts of permanganate were made, then another after 40 minutes, whereafter boiling was continued for 3 hours. After the excess of permanganate had been destroyed by alcohol, the nitrobenzoic acids were extracted in the usual way, except that any portion held back by manganese dioxide was freed by dissolving the latter in sulphurous acid. The *m*-nitrobenzoic acid was exhaustively separated from its isomerides by fractionation of the barium salts (the relatively insoluble *m*-salt crystallising in its characteristic needles), then of the free acids, then again of the barium salts, and so on as often as was necessary. Traces of benzoic acid, only found in Nos. 8 and 9, were determined by the loss in weight of the acid mixture when heated below 100° to constant weight, the sublimed benzoic acid being subsequently identified. Experiment 6 was carried out to ascertain whether the proportions of the isomeric nitrobenzoic acids obtained by oxidation (whereby about 80% of the theoretical quantity was recovered as crude acids) corresponded exactly with the proportions of the isomeric picrates oxidised. This was found to be the case. Corroboration was obtained by oxidising 2 g. of the picrate of the *o*-nitro-compound under identical conditions, whereby 0·579 g. of pure *o*-nitrobenzoic acid was obtained (76% of the theoretical), whereas 2·50 g. of the *m*-isomeride gave 0·76 g. of acid (79·6%); also by boiling 2 g. of *o*-nitrobenzoic acid in 240 c.c. of water with 1·5 g. of potassium hydrogen carbonate and 4 g. of potassium permanganate during 3 hours, whereby 1·789 g. (89·5%) of the unchanged acid was recovered. This proves that, in the particular method employed, undue further oxidation of *o*-, as compared with *m*- and *p*-nitrobenzoic acids, does not occur.

The yields of *m*-compound were calculated in Nos. 1, 7, 8, and 10 on the total separated picrates obtained, less a correction for any excess of picrate (0 to 0·1 g.) used beyond the normal equivalent of 97% of the theoretical quantity, and also for any traces of benzoic acid found and calculated as the picrate of the unnitrated amine. In Nos. 2, 3 and 5, where the picrates of the *op*-mixture had been worked up further for the *p*-compound before its weight was taken, and in No. 9, where this mixture was inadvertently oxidised before

No.	Amine (g.).	Acid (c.c.). H_2SO_4.	Acid (c.c.). HNO_3.	$(NH_4)_2SO_4$.	Separated picrates (g.).	*m*-Picrates (g.).	Picrates oxidised (g.).	*m*-Acid (g.).	*o*- plus *p*-Acids (g.).	Benzoic acid (g.).	*m*-Nitro-compound formed %.
1	1·85	11	0·8	0	4·65	1·87	—	—	—	—	>40·92
2	2·75	15	1·2	10	6·86	2·3	—	—	—	—	>33·1
3	4·647	26	2·1	25	11·65	3·978	—	—	—	—	>33·9
4	5·12	25	2·2	25	13·04	Insufficient separation	—	—	—	—	—
5	1·90	0	6	0	4·64	1·74	—	—	—	—	>36·45
6	—	—	—	—	—	—	1·50 *p*- 0·75 *o*- 0·25 *m*-	0·08	0·72	—	—
7	2·511	15	1·1	0	6·398	2·446	1·79	0·040 pure +0·011 impure	0·440	0	43·95±0·7
8	4·678	25	1·9	25	12·13	3·92	3·28 2·46	0·010 impure 0·008 impure	0·932 0·698	0·026 0·030	33·83±0·35 34·30±0·37
9	3·058	39·7	1·3	0	7·95 Unseparated	3·042	?	0·266 pure 0·01 impure	1·046	0	51·89±0·23
10	3·277	42·2	1·4	0	8·433	3·937	2·24	0·069 pure 0·007 impure	0·490	0	53·51±0·33

its weight had been *accurately* taken, the yield of *m*-compound was calculated on the normal yield of separated picrates amounting to 94% of the theoretical. The proportion of *m*-acid in the separated nitrobenzoic acids gave the percentage of *m*-picrate in the inseparable portion of the picrates.

The ± corrections in the last column of the table are due to adding one-half of the small fraction of impure *m*-nitro-acid to the pure for calculation of the yield. In Nos. 9 and 10 the concentration of the amine in the sulphuric acid was accurately one-half of that obtaining in No. 7. The ammonium sulphate added in Nos. 2, 3, 4, and 8 was in excess of the amount soluble at the nitration temperature. The amount dissolved can be calculated from the following experiment: 15 c.c. of the sulphuric acid and 2·523 g. of the amine gave 17·5 c.c. of solution and 17·3 c.c. at 0°. 6·2 G. of ammonium sulphate gave a clear solution in the above liquid of 20·4 c.c. at 0°; a further 0·2 g. produced a distinct cloudiness (total volume 20·5 c.c.).

The average *m*-nitration in Nos. 9 and 10 is 52·7%. For an average degree of dissociation of 90% in nitration No. 7, Sugden's cubic root dilution law requires a yield of 50·3% of the *m*-compound in Nos. 9 and 10, whereas for 80% and 70% dissociation in No. 7, 51% and 51·9% of the *m*-compound should be obtained in Nos. 9 and 10. Walden's dilution law ($1-\alpha = K/v^{0\cdot45}$) (quoted in Walden, "Leitvermogen der Lösungen," III, 59) requires 52·5, 53·3, and 54·3%, respectively.

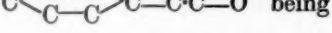
The authors desire to express their indebtedness to the Department of Scientific and Industrial Research for a grant to one of them (E. L. H.) which has enabled him to contribute the experimental portion of this work; also to Sir W. Bragg and the Royal Institution for placing at their disposal the facilities of the Davy Faraday Laboratory, where the work was carried out.

[*Received, March 12th,* 1926.]

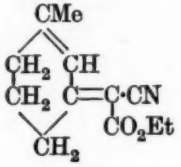
CCIV.—*Properties of Conjugated Compounds. Part I. Conjugative Associations in Extended "Conjugated" Systems.*

By Ernest Harold Farmer and John Ross.

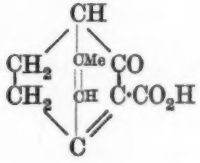
In extended conjugated systems of the type CH:CH·CH:CH·C:O, the characteristic mode of terminal hydrogen addition is usually regarded as due to the conjugative coherence of all the individual unsaturated elements of the chain. Many reactivities of these

structures, however, appear to be dependent on a state of partial association in which the complex CH:CH·C:O acts as a conjugated unit, the whole behaving as a substituted ethylene or as a β-substituted acrylic acid. As a means of estimating the extent of conjugative association in extended systems, an attempt has been made to examine the degree to which the behaviour of the acrylic "unit" is modified by inclusion in systems of the type in question. Since one of the most important properties of the complex is a normal capacity for change from one conjugated form to another (·CH:C·C:O ⇌ :C·C:C·OH)—a change impossible in extended systems unless the olefinic chain is branched—observations have been made in this respect, certain *cyclo*hexenylidenecyanoacetic esters containing the essential structure  being employed for the purpose.

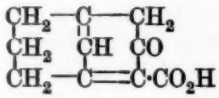
It was shown by Knoevenagel and Mottek (*Ber.*, 1904, **37**, 4464), in their investigation of the reactivity of ketones, that 1-methyl-Δ^1-*cyclo*hexen-3-one reacts with ethyl cyanoacetate in the presence of piperidine, giving ethyl methyl*cyclo*hexenylidenecyanoacetate (I). In accordance with the assigned constitution, this substance could be broken down by hydrolysis with caustic alkali into the original ketone and malonic acid; apparently, however, it was unsuitable for our experiments owing to the ease with which it was stated to undergo an astonishing intramolecular change. Thus, according to these authors, hydrolysis with sodium carbonate yielded an acidic compound to be represented by some such formula as (II) or (III), or one of their enolised equivalents.



(I.)



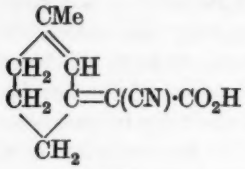
(II.)



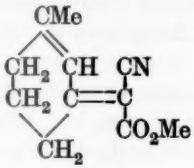
(III.)

Further, the silver salt of the substance yielded with methyl iodide a mixture of isomeric esters or ethers for the isomerism of which it was difficult to account. The formulæ assigned were necessitated solely by the analytical results; there was nothing in the behaviour of the substance itself to suggest the presence of the aromatic nucleus which these formulæ imply. Consequently, in reviewing the evidence, the suspicion arose that the acidic compound was a nitrogenous substance, and, if formula (I) were correct, was actually the normal hydrolysis product (IV). Repetition of Knoevenagel

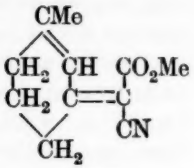
and Mottek's work confirmed this view, thus rendering possible the study of the methyl*cyclo*hexenylidenecyanoacetic esters.



(IV.)



(V.)



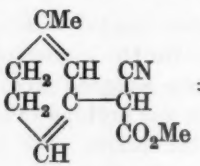
(VI.)

The ethyl ester was very readily obtained and was converted by alcoholic alkali into an acid agreeing with formula (IV) analytically, and in melting point and general properties with Knoevenagel and Mottek's supposed dicyclic compound. This rather intractable acid did not appear homogeneous, but could not be separated into components by fractional crystallisation. Esterification, however, yielded the two isomeric methyl esters mentioned above.

Formula (IV) at once suggests the possibility of geometrical isomerism about the extracyclic double bond, and the two isomerides found might be regarded as the maleinoid and fumaroid forms (V and VI). This being so, these two solid methyl esters should be directly obtainable by the condensation of methyl cyanoacetate with the ketone. When this was done, the excellent yield of the two methyl esters obtained left no doubt as to their monocyclic constitution.

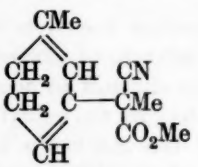
As the isomerides or tautomerides concerned in mobility of the $\alpha\beta$–$\beta\gamma$ type are usually brought into equilibrium in the presence of alkalis or sodium alkyloxides, the two *methyl methyl*cyclo*hexenylidene-cyanoacetates* were separately treated with alcoholic sodium methoxide. In each case, a similar mixture of three esters was obtained from the product. Two of these were the esters (V) and (VI), and the third must be regarded as the methyl methyl*cyclo*hexadienyl-cyanoacetate (VII). Subsequently this was shown to yield a similar mixture of three isomerides on treatment with sodium methoxide. Since in all three mixtures the proportions of the

(VI.) $\rightleftharpoons$



(VII.)

$\rightleftharpoons$ (V.)



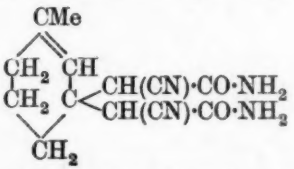
(VIII.)

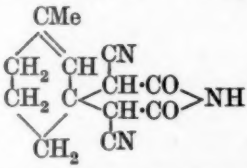
components appeared identical, there is little doubt that an equilibrium holds. Caustic alkali exerted a similar influence during the

hydrolysis of these esters, as was shown by the melting point of the acid mixture obtained and by the nature of the mixture of esters obtained on re-esterification; further, upon repetition of these processes with larger amounts of the ethyl ester first obtained, the third methyl ester was isolated in this case also.

Each of the three esters gave a distinctive dibromide and each could be methylated precisely as the various *cyclo*pentenyl- and *cyclo*hexenyl-cyanoacetic esters and their tautomerides (Harding and Haworth, J., 1910, **97**, 490; Birch and Kon, J., 1923, **123**, 2440), the product in all cases being one and the same methyl derivative (VIII).

In attempts to prepare the cyanoacetamides of the isomeric esters by means of aqueous ammonia, each gave rise to a dicyanoacetamide (IX) and the ammonium salt of the imide (X), both being identical with the compounds directly obtainable from the ketone and cyanoacetic ester by the Guareschi synthesis. Such syntheses resulting from the reversion of a portion of the cyclic ester into its generators, with the subsequent addition of the liberated cyanoacetic ester (or amide) to the undecomposed portion, have recently been observed in other series (private communication by Miss W. Kilroy).

(IX.) 

 (X.)

Among the small portions of ester recovered in these reactions, isomerides other than the original one were obtained. Interconversion of the esters could be secured only by the use of an alkaline equilibrating agent; thus the passage from a fumaroid to a maleinoid form was only possible by way of the third (*cyclo*hexadienyl-) form, and in the original condensation of the ketone and methyl cyanoacetate two and only two forms were obtained.

In estimating the effect of conjugative association on the incorporation of the group CH:CH·C:O in a larger unit, it is convenient to compare the results obtained above with the evidence furnished by substances containing no double bonds other than those of the acrylic system. Among the latter, considerable, and at present inexplicable, variations occur in the speed of attainment and in the position of equilibrium. In some cases, the $\alpha\beta$- and $\beta\gamma$-forms are readily isolable and undergo appreciable interconversion only in the presence of a reagent like sodium alkyloxide; in the limiting cases, isomerisation is so rapid (even in absence of a reagent) and the position of equilibrium favours so strongly one form or the other

that the separation of individuals has been impossible.* In the *cyclo*hexenylidene esters described above, the acrylic group seems to be preserved as a definite unit. Change of the $\alpha\beta$–$\beta\gamma$ type, which might conceivably have been suppressed, is here of normal and intermediate character; and in so far as this is the case there is no positive evidence of any considerable tendency for the extended system, of which the acrylic group is a part, to act persistently as a completely conjugated unit.

Experimental.

Condensation of Methyl Cyanoacetate with 1-*Methyl*-Δ^1-cyclo*hexen*-3-*one*.—A mixture of the ketone (110 g.), the ester (100 g.), and piperidine (10 c.c.) was heated at 120—125° for 6 hours. The cooled product, upon the surface of which a thin aqueous layer had formed, was diluted with ether and thoroughly washed, first with dilute sulphuric acid and then with dilute sodium carbonate solution. The dried ethereal solution was distilled, finally at a very low pressure (the amount of undecomposed material passing over at 1 mm. was double that at 10 mm.); the fraction, b. p. 165—175°/2 mm., solidified on cooling (yield 70%).

A considerable portion of this solid dissolved in boiling petroleum (b. p. 40—60°). The solution deposited one isomeride of *methyl* 1-*methyl*-Δ^1-cyclo*hexenylidene*-3-*cyanoacetate* in large, needle-shaped prisms, m. p. 74°; these were sometimes colourless, but often had a deep yellow colour which was removed by boiling in petroleum solution with animal charcoal (Found: C, 68·95; H, 6·9; N, 7·5. $C_{11}H_{13}O_2N$ requires C, 69·05; H, 6·85; N, 7·3%).

The petroleum mother-liquor, after concentration and cooling, deposited flat, colourless prisms, m. p. 60°. This substance, isomeric with that described above (the two are regarded as isomerides of the fumaroid-maleinoid type), represented about 6% of the ester mixture (Found: C, 69·05; H, 6·9; N, 7·45%).

The portion of the ester mixture undissolved by boiling petroleum crystallised from methyl alcohol–petroleum in colourless, hexagonal prisms, m. p. 88°. The nature of this stable, highly nitrogenous substance, which is readily obtainable from the cyanoacetic ester and piperidine alone, has not been determined (Found: C, 63·1; H, 8·0; N, 17·7%).

* The strictly comparable *cyclo*hexylidene- and *cyclo*pentylidene-cyanoacetic esters are liquids (Birch, Kon, and Norris, J., 1923, **123**, 1368) and from the details published it is evident that both the position of equilibrium and the isolability of the separate forms are uncertain. In the present case, equilibrium is attained when the material is divided between the *cyclo*hexadienyl and the *cyclo*hexenylidene form in the approximate ratio of 3 : 10.

Condensation of Ethyl Cyanoacetate with 1-*Methyl*-Δ^1-cyclo*hexen*-3-*one*.—This condensation, effected by Knoevenagel and Mottek's method (*loc. cit.*), produced an oil from which, by distillation at 1 mm. pressure and refractionation, a mixture of esters, b. p. 190°/16 mm., which solidified on cooling, was obtained. The main part of this mixture melted at 58° after recrystallisation from light petroleum. This substance, doubtless one form of ethyl methyl-*cyclo*hexenylidenecyanoacetate, was used for the repetition of Knoevenagel and Mottek's experiments (Found: C, 70·0; H, 7·5; N, 7·05. Calc. for $C_{12}H_{15}O_2N$: C, 70·2; H, 7·4; N, 6·85%).

Equilibration by Alcoholic Caustic Alkali.—Hydrolysis of methyl-cyclo*hexenylidenecyanoacetic esters*. The ethyl ester was not appreciably hydrolysed on boiling for 12 hours with 15% hydrochloric acid and was only slowly affected by boiling with sodium carbonate solution in the manner described by Knoevenagel and Mottek. Since prolonged treatment with caustic alkali caused degradation, the ester was boiled for 30 minutes with 10% aqueous-alcoholic caustic potash (alcohol : water = 3 : 1). The deep brown solution so obtained was cooled, and the hydrolysis product separated by the usual methods into neutral and acidic portions. The acidic portion was a very sticky, brown solid which was recrystallised several times from benzene, decolorised by animal charcoal, and recrystallised from acetone. This acid, which was not homogeneous in crystalline form, melted at 149° (Found: C, 67·6; H, 6·3; N, 7·9; *M*, monobasic, 174. Calc. for $C_{10}H_{11}O_2N$: C, 67·8; H, 6·25; N, 7·9%; *M*, 177·1). The *ammonium* salt was obtained, from the acid and ammonia in ether, as a colourless, crystalline precipitate, which was dried in a vacuum. The *silver* salt was precipitated as a pale yellow powder from an aqueous solution of the ammonium salt by silver nitrate.

Separation of the isomeric esters. The mixture of methyl esters, b. p. 180—185°/17 mm., obtained by boiling the silver salt with alcoholic methyl iodide was crystallised from petroleum. The characteristic, needle-like crystals of methyl methyl*cyclo*hexenylidenecyanoacetate, m. p. 74°, separated first; then, after concentration, the geometrical isomeride, m. p. 60°, was obtained in large, hexagonal plates. (Both of these were shown by analysis and by direct comparison to be identical with the respective esters described above.) Finally, when the mother-liquor had been evaporated almost to dryness, crystals of *methyl* 1-*methyl*-$\Delta^{1:3}$-cyclo*hexadienyl*-3-*cyanoacetate* were obtained. These, after recrystallising several times from strongly-cooled methyl alcohol–petroleum, were obtained in colourless needles, m. p. 42° (Found: C, 69·1; H, 7·0; N, 7·5. $C_{11}H_{13}O_2N$ requires C, 69·05; H, 6·9; N, 7·35%).

The proportions in which the three esters were obtained were (m. p. 74°) : (m. p. 60°) : (m. p. 42°) = 4 : 1 : 1·6.

Equilibration by Sodium Alkyloxide.—A mixture of the ester, m. p. 74° (3 g.) and sodium methoxide (1 mol.) in cold methyl alcohol was kept for one hour and then poured into water. The mixture of solid esters (2 g.) obtained by extracting the product with ether yielded, on fractional crystallisation, the three isomeric esters in the approximate proportions 4·2 : 1 : 1·5. Nearly a third of the material suffered hydrolysis during the process.

Similar results were obtained with the other two isomerides.

Methylation of the Isomeric Esters.—An equilibrated mixture obtained as described above was heated on a water-bath with an excess of methyl iodide for 30 minutes. The cooled solution was poured into ice-water, and the product extracted with ether. The extract was washed in turn with dilute acid and sodium carbonate solution and dried. Evaporation of the ether yielded an oil two-thirds of which distilled at 160—165°/10 mm. On redistillation it was obtained as a colourless, mobile liquid, b. p. 160°/11 mm. This substance, from its analysis and ready conversion into the corresponding acetonitrile, must be regarded as *methyl* 1-*methyl*-$\Delta^{1:3}$-cyclo*hexadienyl*-3-α-*cyanopropionate* (VIII) (Found : C, 69·95; H, 7·5; N, 7·3. $C_{12}H_{15}O_2N$ requires C, 70·2; H, 7·4; N, 6·9%).

*Bromination of the Isomeric Methyl Methyl*cyclo*hexenylidene-cyanoacetates.*—The esters, m. p. 74° and 60°, yielded, on bromination (1 mol.) in cold chloroform, *dibromides* which crystallised from alcohol–petroleum in large, colourless prisms, m. p. 77° (Found : Br, 45·2%), and fine needles, m. p. 65° (Found : Br, 45·3. $C_{11}H_{13}O_2NBr$ requires Br, 45·5%) respectively. The ester, m. p. 42°, similarly yielded a yellow, oily dibromide (Found : Br, 44·8%).

These dibromides readily lost hydrogen bromide on treatment with diethylamine, but the products were all liquid and could not be satisfactorily reduced by any of the reagents employed.

Decarboxylation of the Cyano-esters.—Decarboxylation of (VIII) by Birch and Kon's method (*loc. cit.*, p. 1374) gave, in good yield, 1-*methyl*-$\Delta^{1:3}$-cyclo*hexadienyl*-3-*propionitrile* as a colourless, mobile liquid, b. p. 126°/11 mm. (Found : C, 81·9; H, 9·0; N, 9·0. $C_{10}H_{13}N$ requires C, 81·6; H, 8·9; N, 9·5%).

The purified hydrolysis product of methyl (or ethyl) methyl*cyclo*hexenylidenecyanoacetate (p. 1575) yielded, on heating with water at 180° or on boiling for 30 minutes with 15% hydrochloric acid, a light, neutral oil which, after extraction, drying, and distillation, was obtained as a colourless, mobile, highly refractive liquid, b. p. 118°/10 mm. (Found : C, 80·8; H, 8·3; N, 10·2. $C_9H_{11}N$ requires C, 81·1; H, 8·3; N, 10·5%).

Action of Ammonia upon the Three Isomeric Esters.—The methyl ester, m. p. 74° (3 g.), gradually dissolved in concentrated aqueous ammonia, and after 12 hours large crystals, m. p. 273°, of 1-*methyl*-Δ^1-cyclo*hexene*-3 : 3-*dicyanoacetamide* (IX) were deposited. A second crop consisted of this substance and the *ammonium* salt of the cyanimide (X). The latter had m. p. 188° (Found : C, 60·1; H, 6·4; N, 21·3. $C_{13}H_{16}O_2N_4$ requires C, 59·95; H, 6·2; N, 21·5%) and yielded, on acidification of its aqueous solution, the free *imide*, a white, crystalline powder, m. p. 195° (Found : N, 17·1. $C_{13}H_{13}O_2N_3$ requires N, 17·3%). The dicyanoacetamide, which was insoluble in all the ordinary solvents, was washed in turn with boiling alcohol and boiling water and then had m. p. 275° (Found : C, 59·85; H, 6·2; N, 21·4. $C_{13}H_{16}O_2N_4$ requires C, 59·95; H, 6·2; N, 21·5%). The yields of the condensation products corresponded with the explanation of their formation given in the introduction.

The esters, m. p. 60° and m. p. 42°, also gave on similar treatment the same two compounds (m. p. 188° and m. p. 275°). The quantities of the cyclic imide and dicyanoacetamide produced varied in the different experiments, but the total amount was constant.

*Condensation of Methyl Methyl*cyclo*hexenylidenecyanoacetate with Methyl Cyanoacetate.*—To a solution of the ester, m. p. 74° (5 g.) and methyl cyanoacetate (2·5 g.) in cold alcohol, ammoniacal alcohol (10 c.c., saturated at −10°) was added, and the mixture kept at 0° for 2 days, much crystalline matter separating. The ammonium salt of the cyclic imide and the dicyanoacetamide described above were thus obtained in 68% yield.

*Condensation of Methyl*cyclo*hexenone and Ethyl Cyanoacetate.*—A mixture of methyl*cyclo*hexenone (4 g.), ethyl cyanoacetate (8·5 g.), and ammoniacal alcohol (18 c.c., saturated at −10°) was kept at 0° in a closed bottle. The crystals deposited after 1 day consisted almost entirely of cyanoacetamide, but after 3 days 5·5 g. of the almost pure ammonium salt of the imide (X) were obtained.

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CCV.—*The Isomerism of the Styryl Alkyl Ketones. Part III. Methoxy-2- and 4-hydroxystyryl Alkyl Ketones.*

By ALEXANDER McGOOKIN and DONALD JAMES SINCLAIR.

IN order to confirm the results of the investigations on the isomerism and behaviour towards alkali of the hydroxystyryl alkyl ketones (J., 1924, **125**, 2099; 1925, **127**, 2539) various derivatives of 2-hydroxystyryl methyl ketone and analogous compounds have been prepared and examined.

5-Methoxy-2-hydroxystyryl methyl ketone (Heilbron and Whitworth, J., 1923, **123**, 238), like the 2-hydroxy-compound, exists in a yellow and a colourless form of identical m. p. and is partly converted into the red *sodium* salt of 5 : 5′-*dimethoxy*-2 : 2′-*dihydroxydistyryl ketone* in alkaline solution. This change occurs instantly with the yellow isomeride, but only very slowly with the colourless modification; the colourless form of 2-hydroxystyryl methyl ketone also develops the usual red colour in similar circumstances.

The colourless form of 4-methoxy-2-hydroxystyryl methyl ketone has been isolated; it is stable in air and resembles the colourless form of 2-hydroxystyryl methyl ketone in properties. The yellow form (Heilbron and Whitworth, *loc. cit.*) has not been obtained pure and is under investigation.

The yellow crystalline condensation product, m. p. 83°, of 3-methoxysalicylaldehyde and acetone obtained by Heilbron and Whitworth (*loc. cit.*), and regarded by them as β-hydroxy-β-3-methoxy-2-hydroxyphenylethyl methyl ketone, has also been described by Nomura and Nozawa (*Sci. Rep. Tôhoku Imp. Univ.*, 1918, **7**, 79), who consider it a hydrate of 3-methoxy-2-hydroxystyryl methyl ketone. Further examination indicates that it is a hydrate rather than an aldol. In addition to the benzoyl derivative of 3-methoxy-2-hydroxystyryl methyl ketone already obtained from it by Heilbron and Whitworth (*loc. cit.*) an *acetyl* derivative of the unsaturated ketone has been prepared. Both compounds, on hydrolysis, yield the hydrated substance. Moreover, condensation of this compound with 3-methoxysalicylaldehyde produces the symmetrical distyryl ketone. Again, crystallisation of the hydrated substance from dry benzene yields, as a second crop, colourless needles which, on removal of the solvent, immediately absorb water to form the original yellow compound of m. p. 83°. 3-Methoxy-2-hydroxystyryl methyl ketone, however, could not be isolated. From the compound of m. p. 83°, by crystallisation from an anhydrous solvent, Nomura and Nozawa (*loc. cit.*) obtained

an unsaturated ketone of m. p. 77—77·5°. This m. p. for 3-methoxy-2-hydroxystyryl methyl ketone is anomalous in three respects: (i) all ketones of this type melt at about 130°; (ii) removal of water from an aldol or a hydrate invariably causes a rise in m. p.; (iii) the symmetrical distyryl ketone has a normal m. p.

In Part I the compound of m. p. 83° was assumed to have the aldol structure, and the fact that it could not be isomerised was taken as evidence of the geometric nature of the isomerism of this class of ketones. In view of the present observations this evidence cannot be taken as conclusive.

The yellow form of 3-methoxy-4-hydroxystyryl methyl ketone (Francesconi, *Gazzetta*, 1908, **38**, ii, 70; McGookin and Heilbron, J., 1924, **125**, 2104) is peculiar in being exceedingly stable, resisting isomerisation except by extreme methods. When, however, concentrated alkali is added to its alkaline solution, the salt precipitated is that of the colourless form. Hence it is assumed that the salts of both isomerides are in equilibrium in alkaline solution.

The yellow form of 3-methoxy-4-hydroxystyryl methyl ketone changes on fusion into the colourless modification of the same m. p. —a similar change doubtless accounts for the identity of the m. p.'s of each pair of isomerides throughout this series of ketones. Both forms of this substance resemble those of 2-hydroxystyryl methyl ketone by dissolving in alkali, the yellow form to yield a red solution and the colourless isomeride to give a yellow solution which assumes a red colour on standing. In both instances the red colour is due to the *sodium* salt of 3 : 3′-*dimethoxy*-4 : 4′-*dihydroxydistyryl ketone*. Hence styryl methyl ketones are capable of condensing to a slight extent with 4-hydroxyaldehydes in the presence of alkalis (compare Buck and Heilbron, J., 1922, **121**, 1095).

Experimental.

5-*Methoxy*-2-*hydroxystyryl Methyl Ketone*.—The colourless modification was obtained, by boiling the yellow isomeride (Heilbron and Whitworth, *loc. cit.*) with water containing a trace of acid, in needles, m. p. 124°, soluble in alcohol or benzene. It dissolves in alkali to a yellow solution which develops a deep red colour after 12 hours (Found : C, 68·5; H, 6·3. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%).

5 : 5′-*Dimethoxy*-2 : 2′-*dihydroxydistyryl Ketone*.—When 40% sodium hydroxide (10 c.c.) was added to a solution of the yellow isomeride of 5-methoxy-2-hydroxystyryl methyl ketone (2 g.) in 20% sodium hydroxide (30 c.c.), lustrous, green needles separated. An aqueous solution of these, on acidification, gave the distyryl ketone (1·2 g.), which crystallised from alcohol in orange needles,

m. p. 158°, soluble in acetone but almost insoluble in benzene (Found: C, 69·6; H, 5·6. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5%).

4-*Methoxy*-2-*hydroxystyryl Methyl Ketone.*—The following is the best modification of Heilbron and Whitworth's method. To a solution of 4-methoxysalicylaldehyde (9 g.) and acetone (16 g.) in alcohol (100 c.c.), sodium hydroxide (200 c.c. of 20%) was added. After 3 days the red mixture was diluted with water (1000 c.c.), cooled to 0°, and almost neutralised with dilute sulphuric acid (rise of temperature or excess of acid caused the production of tar). The product (10 g.) was crystallised from benzene and from chloroform–hexane and obtained in colourless needles, m. p. 131°. It was readily soluble in alkali to a yellow solution which developed a deep red colour after 12 hours.

4 : 4′-*Dimethoxy*-2 : 2′-*dihydroxydistyryl Ketone.*—A mixture of 2 mols. of 4-methoxysalicylaldehyde (10 g.), 1 mol. of acetone (2 g.), and alcohol (40 c.c.) was treated with sodium hydroxide (250 c.c. of 20%) and warmed on the water-bath for 10 minutes. The deep red solution deposited, after 12 hours, lustrous green needles of the *sodium* salt of the distyryl ketone. From an aqueous solution of this, almost neutralised at 0°, the *ketone* was precipitated as a yellow solid. It crystallised from cold aqueous alcohol in brown plates, m. p. 170°, soluble in alcohol, but almost insoluble in benzene. It is unstable and produces a red solution with an intense green fluorescence when warmed in alcohol (Found: C, 69·6; H, 5·6. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5%).

3-*Methoxy*-2-*hydroxystyryl Methyl Ketone Hydrate* (?).—This compound (Heilbron and Whitworth, *loc. cit.*) formed yellow plates, m. p. 83°, from aqueous alcohol. It crystallised from dry benzene in similar yellow plates, but the second crop of crystals consisted of colourless, hygroscopic needles. These dissolved in alkali to form an orange-red solution which developed the usual deep red colour on standing.

3-*Methoxy*-2-*acetoxystyryl Methyl Ketone.*—The hydrated compound (10 g.) was boiled for an hour with acetic anhydride (150 c.c.), the hot solution poured into an excess of water, and almost neutralised with sodium carbonate. The precipitate produced (10 g.) crystallised from alcohol in colourless needles, m. p. 91°, soluble in benzene or hot water (Found: C, 66·4; H, 6·1. $C_{13}H_{14}O_4$ requires C, 66·6; H, 6·0%).

3 : 3′-*Dimethoxy*-2 : 2′-*dihydroxydistyryl Ketone.*—The sodium salt that separated after 24 hours from a solution of 3-methoxysalicylaldehyde (50 g.) in acetone (80 g.) and sodium hydroxide (600 c.c. of 2·5%) to which 10% sodium hydroxide (240 c.c.) had been added was dissolved in water and acidified. The ketone precipitated

crystallised from aqueous alcohol in orange needles, m. p. 182° (Found: C, 69·6; H, 5·5. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5%).

3-Methoxy-4-hydroxystyryl Methyl Ketone.—A solution of vanillin (50 g.) in acetone (120 c.c.) and alcohol (50 c.c.) was treated with sodium hydroxide (100 c.c. of 20%) and kept for 12 hours. Long, yellow needles of the *sodium* salt of the colourless isomeride were produced; the *ketone* obtained from these crystallised from aqueous alcohol in colourless needles, m. p. 129°, soluble in acetone or benzene. It dissolved in alkali to a yellow solution which turned red after 12 hours.

*3 : 3′-Dimethoxy-4 : 4′-dihydroxydistyryl Ketone.**—(a) On boiling, a solution of the preceding colourless isomeride (25 g.) in sodium hydroxide (200 c.c. of 20%) became deep red and acetone was evolved. When the evolution of this had ceased, after 15 minutes, the solution was cooled, and sodium hydroxide (40%) added until a precipitate formed. Lustrous green needles of the *sodium* salt of the distyryl ketone slowly separated. The *ketone* obtained from these crystallised from chloroform in pale yellow needles, m. p. 142° (Found: C, 69·6; H, 5·6. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5%).

This compound was very soluble in alcohol or acetone, moderately easily soluble in chloroform, but almost insoluble in benzene. It forms an orange-red *hydrate*, m. p. 121°, containing one molecule of water when crystallised from an aqueous solvent (Found: C, 65·8; H, 5·9. $C_{19}H_{18}O_5,H_2O$ requires C, 66·2; H, 5·8%). The hydrate loses water when heated in a steam-oven or crystallised from a non-aqueous solvent.

(b) A better yield (15 g.) of the distyryl ketone was obtained by gradually adding concentrated hydrochloric acid (50 c.c.) to a solution of vanillin (25 g.) in acetone (90 c.c.) cooled in a freezing mixture. A dark violet-red coloration was observed and from the mixture, kept at 0° for 4 days, green-black crystals separated. These were filtered off, washed well with ether, and decomposed by dissolution in excess of sodium hydroxide (10%). The free distyryl ketone was obtained from this solution as before.

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* This compound has recently been prepared by Nomura and Hotta (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 119).

CCVI.—*The Halogenation of Phenols.*

By FREDERICK GEORGE SOPER and GILBERT FREEMAN SMITH.

THE iodination of phenols has been investigated by Cofman (J., 1919, **115**, 1040), who concluded that the active iodinating agent was hypoiodous acid, free iodine having apparently no direct iodinating effect. Similar views were held on the mechanism of bromination (Baines, J., 1922, **121**, 2810), but recently Francis (*J. Amer. Chem. Soc.*, 1925, **47**, 2340) has shown that bromine is a more active brominating agent than hypobromous acid. Both Cofman and Francis are of the opinion that probably the only active halogenating agent is the positive halogen ion. This conclusion can be tested using halogens and hypohalous acids, since, although the actual degrees of ionisation of these substances into positive halogen ions (Stieglitz, *J. Amer. Chem. Soc.*, 1901, **23**, 796) are not known—except in the case of hypoiodous acid (Murray, J., 1925, **127**, 882)—their relative ionisations may be calculated from other data. For, assuming the existence of such equilibria as

$$HOCl \rightleftharpoons OH' + Cl^{\cdot}$$
$$Cl_2 \rightleftharpoons Cl' + Cl^{\cdot}$$

then

$$\frac{K_{HOCl}}{K_{Cl_2}} = \frac{[OH'][Cl^{\cdot}]}{[HOCl]} \Big/ \frac{[Cl'][Cl^{\cdot}]}{[Cl_2]} = \frac{[Cl_2][OH'][H^{\cdot}]}{[Cl'][HOCl][H^{\cdot}]} = \frac{K_w}{K_J},$$

where K_J is the hydrolysis constant of chlorine (Jakowkin, *Z. physikal. Chem.*, 1899, **29**, 613) and equals $4{\cdot}84 \times 10^{-4}$. Similar expressions hold for bromine and for iodine, the hydrolysis constants being $5{\cdot}2 \times 10^{-9}$ and 3×10^{-13} respectively (Bray and Connolly, *J. Amer. Chem. Soc.*, 1911, **33**, 1485; Bray, *ibid.*, 1910, **32**, 932). On substituting these values in the above expression, the ionisation constants of chlorine and hypochlorous acid will be in the ratio $4{\cdot}5 \times 10^{10}$ to 1; and one would expect that their chlorinating efficiencies would be in the same ratio. The corresponding values for bromine and iodine and their hypohalous acids are 5×10^5 and 30 respectively. Thus, whilst hypochlorous acid would have little chlorinating effect in comparison with free chlorine, we should expect the effects of iodine and hypoiodous acid to be of the same order of magnitude.

In order to test this theory of halogenation by positive halogen ion, the chlorination of phenols has been studied, using hypochlorous acid and chlorine as chlorinating agents. The much greater stability of hypochlorous acid (as compared with hypobromous and hypoiodous acids) has allowed of a sharp differentiation between the mechanisms of substitution of phenols by these two chlorinating agents.

The mechanism of the interaction with hypochlorous acid was investigated by the isolation method. The reaction speed is approximately proportional to the phenol and hypochlorous acid concentrations, and is greatly affected by the alkalinity or acidity of the mixture. In acid and in dilute alkaline solutions (hydroxyl-ion concentration in the neighbourhood of 10^{-7}) the reaction speed increases in direct proportion to the hydroxyl-ion concentration until it becomes too rapid for measurement. In more strongly alkaline solution (hydroxyl-ion concentration about 10^{-2}), the speed decreases to measurable dimensions, and is now inversely proportional to the hydroxyl-ion concentration.

These facts can be interpreted in two ways. Interaction may take place either between the phenol molecule and the hypochlorite ion or between hypochlorous acid and the phenoxide ion, the reaction speed being given by the alternative equations

$$v = k_2'[\mathrm{OCl'}][\mathrm{PhOH}] \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$v = k_2[\mathrm{HOCl}][\mathrm{PhO'}] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

On both hypotheses addition of alkali, by causing increased ionisation, would first increase and then decrease the speed as was observed. The alternative hypotheses cannot, however, be differentiated by studying the reaction between a simple phenol and hypochlorous acid, since it follows from the ionic equilibria of hypochlorous acid and a phenol that

$$[\mathrm{OCl'}][\mathrm{PhOH}]/[\mathrm{HOCl}][\mathrm{PhO'}] = K_a'/K_a'' = \text{constant},$$

where K_a' and K_a'' are the respective ionisation constants. It is obvious that any test of the first explanation will be equally satisfactory when applied to the second explanation, if it is based on the constancy of k_2 or k_2'.

It is shown later from other evidence that the mechanism involves the phenoxide ion and hypochlorous acid. The constant k_2, rather than k_2', is therefore calculated in the following preliminary proof of the correctness of the suggested mechanism of the reaction.

The calculation of the velocity coefficient in the presence of excess of alkali involves the hydrolysis constant of sodium hypochlorite (Soper, J., 1924, **125**, 2227), since the hypochlorous acid and the phenol are present almost entirely as ions, sodium hypochlorite and phenoxide in the presence of $N/10$-hydroxyl-ion being hydrolysed only to the extent of 0·1 and 0·001% respectively.

$$dx/dt = k_2[\mathrm{HOCl}][\mathrm{PhO'}] = k_2K_h'/[\mathrm{OH'}]\,.\,[\mathrm{OCl'}][\mathrm{PhO'}]$$
$$= k_2K_h'/[\mathrm{OH'}]\,.\,(b-x)(a-x)$$

or
$$\frac{k_2K_h'}{[\mathrm{OH'}]} = \frac{1}{t(a-b)}\ln\frac{b(a-x)}{a(b-x)}$$

where K_h' represents the hydrolysis constant of the hypochlorite.

The terms $a - x$ and $b - x$ in this equation represent the activities of the hypochlorite and phenoxide ions which are some fraction of the concentrations of sodium hypochlorite and phenoxide, respectively, dependent on the ionic strength (Lewis and Randall, "Thermodynamics," 1924) of the mixture. In the absence of data on the activities of these ions, we have taken them as equal to the concentrations of their respective salts. The effective concentration of the hydroxyl ion was taken as the product of the concentration of free base and its appropriate activity coefficient. The results obtained at 25·0° with *p*-cresol and alkaline hypochlorite are in Table I, where time is shown in minutes.

TABLE I.

[HOCl] = 10^{-3}; [*p*-cresol] = 2×10^{-3}; [NaOH] = 0·019; γ[OH′] = 0·01424.			[HOCl] = 10^{-3}; [*p*-cresol] = 2×10^{-3}; [NaOH] = 0·038; γ[OH′] = 0·02904.		
Time.	[OCl′] $\times 10^4$.	$k_2 \times 10^{-5}$.	Time.	[OCl′] $\times 10^4$.	$k_2 \times 10^{-5}$.
0	8·28	—	0	8·90	—
4·03	5·51	8·59	3·40	7·44	8·39
6·78	4·26	8·75	7·88	5·95	8·59
9·67	3·19	9·26	11·65	4·93	8·82
13·08	2·13	10·3	15·75	4·03	9·10
17·15	1·48	10·5	21·03	3·07	9·60
			27·23	2·24	10·1

Another experiment, in which [HOCl] = 10^{-3}; [*p*-cresol] = 10^{-2}; [NaOH] = 10^{-1}; γ[OH′] = 0·0712, gave values of $k_2 \times 10^{-5}$ which gradually decreased from 9·37 to 8·70.

The velocity coefficient can also be calculated from measurements of the reaction speed in water. The ionisation constants of hypochlorous acid (Soper, *loc. cit.*) and of *p*-cresol (Boyd, J., 1915, **107**, 1538) are $1·0 \times 10^{-8}$ and $0·67 \times 10^{-10}$, respectively. The hydrogen-ion concentration will therefore be governed by the hypochlorous acid, and in *M*/1000-solution will be $3·1 \times 10^{-6}$, but will increase slightly in concentrated solutions of *p*-cresol. During the reaction, hypochlorous acid disappears, and it might be anticipated that the acidity of the mixture would diminish. Actually indicators show that at the conclusion of the reaction the acidity has slightly increased. This is probably due to a very slight reduction of the hypochlorous acid, for even traces of hydrochloric acid would materially affect the hydrogen-ion concentration. In the calculations which follow, the hydrogen-ion concentration has been regarded as constant.

In aqueous solution both hypochlorous acid and *p*-cresol are mainly un-ionised. The concentration of the phenoxide-ion will be

determined by the acidity of the solution and the ionisation constant of the cresol, thus

$$[R{\cdot}O'] = K_a''[R{\cdot}OH]/[H^+].$$

The velocity is given by

$$dx/dt = k_2[R{\cdot}O'][HOCl] = k_2[HOCl]{\cdot}K_a''[R{\cdot}OH]/[H^+] = k_2K_a''(b-x)(a-x)/[H^+]$$

or

$$\frac{k_2K_a''}{[H^+]} = k = \frac{1}{t(a-b)}\ln\frac{b(a-x)}{a(b-x)}.$$

Mixtures were used in which the hypochlorous acid was $M/1000$, and the *p*-cresol-concentration varied from 10^{-3} M to 4×10^{-2} M. Table II shows one experiment in detail, and Table III summarises all the experiments.

Table II.

$[R{\cdot}OH] = 10^{-2}$; $[HOCl] = 10^{-3}$.

Time.	$[HOCl] \times 10^3$.	$k_2K_a''/[H^+]$.
0	0·821	—
3·60	0·583	9·81
6·85	0·449	9·16
7·97	0·402	9·39
9·57	0·362	8·96

TABLE III.

$[R{\cdot}OH] \times 10^3$.	k.	$[H^+] \times 10^6$.	$k_2 \times 10^{-5}$.
1	19·5	3·17	9·23
2	13	3·19	6·19
5	10	3·22	4·81
10	9·3	3·26	4·53
20	8·8	3·37	4·43
40	8·0	3·55	4·24

The higher value for the velocity coefficient when equimolar quantities of hypochlorous acid and cresol interact is due to the chlorination of the chlorocresol formed. The average value for the velocity coefficient in aqueous solution when excess of the cresol is present may be taken as 5×10^5, as compared with the value 10×10^5 in alkaline solution. The lower value obtained in water is probably to be attributed partly to the fact that activities are not accurately represented by concentrations, partly to some uncertainty in the ionisation constants concerned, and partly to the effect of the presence of other substances on the degrees of ionisation.

The addition of acids, with the exception of hydrochloric acid, decreased the observed speed. The effect of hydrochloric acid doubtless depends on the formation of chlorine, and is dealt with in Section 2.

The comparison of velocity coefficients calculated from the observed speeds in aqueous and in strongly alkaline solution is a stringent test of the mechanism, as it involves concentrations of the reacting species which differ by several thousand times in the two cases. This test has been repeated for other phenols. The results are summarised in Table IV.

TABLE IV.

[R·OH].	[HOCl].	[H·] × 10⁶.	[NaOH].	γ[OH'].	k_2.
Phenol ($K_a'' = 1{\cdot}1 \times 10^{-10}$).					
0·005	0·0010	3·24	—	—	$3{\cdot}24 \pm 0{\cdot}27 \times 10^5$
0·010	0·0010	—	0·10	0·0712	$3{\cdot}34 \pm 0{\cdot}07 \times 10^5$
0·010	0·0010	—	0·04	0·0249	$3{\cdot}21 \pm 0{\cdot}08 \times 10^5$
o-*Chlorophenol* ($K_a'' = 7{\cdot}7 \times 10^{-10}$).					
0·004	0·0010	3·61	—	—	$10{\cdot}6 \pm 0{\cdot}7 \times 10^4$
0·010	0·0010	—	0·10	0·0712	$5{\cdot}9 \pm 0{\cdot}1 \times 10^4$
m-*Cresol* ($K_a'' = 0{\cdot}98 \times 10^{-10}$).					
0·002	0·0010	3·19	—	—	$3{\cdot}50 \pm 0{\cdot}18 \times 10^6$
0·002	0·0005	—	0·50	0·373	$4{\cdot}38 \pm 0{\cdot}03 \times 10^6$
o-*Nitrophenol* ($K_a'' = 7{\cdot}5 \times 10^{-8}$).					
0·004	0·0010	18·3	—	—	$1{\cdot}65 \pm 0{\cdot}13 \times 10^3$
0·010	0·0010	—	0·015	0·004	$1{\cdot}01 \pm 0{\cdot}02 \times 10^3$
p-*Nitrophenol* ($K_a'' = 9{\cdot}6 \times 10^{-8}$).					
0·010	0·0010	31·0	—	—	$1{\cdot}40 \pm 0{\cdot}10 \times 10^3$
0·010	0·0010	—	0·015	0·004	$0{\cdot}68 \pm 0{\cdot}03 \times 10^3$

The agreement between the velocity coefficients calculated over such exceptionally wide ranges of concentration is satisfactory and shows that the mechanism proposed is of general character; moreover, it eliminates the possibility of concurrent interaction of the hypochlorite ion with the phenoxide ion.

In order to differentiate between the two possible mechanisms of chlorination of a phenol by hypochlorous acid, the chlorination of salicylic acid has been studied. Here the alternative mechanisms become

$$v = k_2'[\mathrm{HO{\cdot}C_6H_4{\cdot}CO_2H}][\mathrm{OCl'}] \quad . \quad . \quad . \quad . \quad (3)$$

$$v = k_2[\mathrm{'O{\cdot}C_6H_4{\cdot}CO_2'}][\mathrm{HOCl}] \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In this case, unlike that of a simple phenol, the expression representing k_2/k_2' is not constant, but is inversely proportional to the hydroxyl-ion concentration. It is therefore possible, by examination of the speed of reaction in media of different hydroxyl-ion concentrations, to differentiate between the two theories, for on one mechanism only will velocity coefficients be obtained which are independent of the alkalinity of the medium.

The second ionisation constant of salicylic acid (Senter and Bulle, J., 1912, **101**, 2532) is approximately 1×10^{-13}. In $N/10$-hydroxyl ion the disodium salt is 50% hydrolysed, and in N-hydroxyl ion 9% hydrolysed. If the interaction involves the hypochlorite ion, then the speed, on change of the alkalinity from $N/10$ to N, will be decreased 55 times,* whilst if the phenoxide ion is involved the

* The ratio of undissociated acid to monosodium salt is decreased 10 times and the monosodium salt concentration is decreased 5·5 times, giving a total decrease in the concentration of the undissociated acid of 55 times. The hypochlorite-ion concentration remains unaltered. The calculation is approximate, as the activities are not known.

corresponding decrease will be certainly less than 10 times (due to a 10-fold decrease in the un-ionised hypochlorous acid) since the concentration of the phenoxide ion has been increased 1·8 times, giving a net decrease of 5·5 times. Actually the observed decrease is 2·7 times, which is in favour of the phenoxide-ion theory.

TABLE V.

[Salicylic acid] = 10^{-2}; [HOCl] = 10^{-3}; $v = d[OCl']/dt$ (in mols./min.).

	[NaOH] = 0·10.		[NaOH] = 0·20.		[NaOH] = 1·00.	
[OCl′] × 10^3.	t.	$v \times 10^5$.	t.	$v \times 10^5$	t.	$v \times 10^5$.
0·9	2·00	1·53	2·00	1·24	7·75	0·59
0·8	8·90	1·39	10·25	1·18	25·60	0·51
0·7	16·75	1·18	19·00	1·05	46·00	0·44
0·6	26·00	1·06	29·85	0·90	100·00	0·37

Further confirmation of the theory that the reaction involves the phenoxide ion is obtained from the behaviour in the initial stages of the reaction. The phenomenon is particularly clearly defined with *p*-nitrophenol, but is of general occurrence. If sodium hypochlorite is mixed with the phenol, the reaction proceeds smoothly without initial disturbance. If, however, sodium phenoxide be mixed with hypochlorous acid, as much as 35% of the hypochlorous acid may disappear before a portion of the solution can be removed for titration. The reaction after the initial disturbance is normal. The initial fall of titre in the one case is obviously due to the high concentrations of hypochlorous acid and phenoxide ion. An example of this effect is given in Table VI.

TABLE VI.

HOCl (10^{-3}) added to *p*-nitrophenol (10^{-2}) and NaOH (1·5 × 10^{-2}).		*p*-Nitrophenol (10^{-2}) added to HOCl (10^{-3}) and NaOH (1·5 × 10^{-2}).	
Time.	[OCl′] × 10^4.	Time.	[OCl′] × 10^4.
0	10	0	10
0·93	6·44	0·93	9·74
4·97	6·29	4·63	9·60
12·00	6·17	27·97	9·11

2. *Chlorination of Phenols and Phenolic Ethers by Chlorine.*

The presence of small traces of hydrochloric acid has a great effect on the speed of interaction of hypochlorous acid and a phenol. The speed is independent of the concentration and nature of the phenol, and is dependent on the hypochlorous acid concentration and the square of the hydrochloric acid concentration, thus :

$$v = k_1[H^+][Cl^-][HOCl] = k_1[HCl]^2[HOCl] \quad . \quad . \quad . \quad (5)$$

It is obvious that the speed measured is that of the formation of chlorine from hydrochloric and hypochlorous acids,* the chlorine immediately reacting with the phenolic substance present. Using *p*-nitrophenol, a slower speed is observed, but on increasing its concentration the same limiting speed is obtained. Chlorine, therefore, chlorinates a phenol more rapidly than does hypochlorous acid. Some of the observed results obtained at 25·0° are in Table VII.

TABLE VII.

$[HCl] = 2 \times 10^{-4}$; $[HOCl] = 10^{-3}$.

Substance.	*p*-Cresol.	Phenol.	Phenetole.	Anisole.	*p*-Nitrophenol.
Conc. to give limiting speed	$<2 \times 10^{-3}$	$<2 \times 10^{-3}$	4×10^{-3}	10^{-2}	10^{-2}
$k \times 10^{-3}$	2·17	2·14	2·16	2·14	2·06

The velocity coefficient is unimolecular, since the concentration of the hydrochloric acid is constant, each molecule of chlorine which reacts with the phenol giving one molecule of hydrochloric acid, which in turn forms chlorine.

3. *The Action of Hypochlorous Acid on Phenolic Ethers.*

In dilute alkali, in which the existence of chlorine is excluded, no fall in titre of the mixture of ether and hypochlorous acid is observed. In water, however, a slow reaction occurs, the rate of which is only slightly dependent on the concentration of the ether present, and is thus probably due to chlorine. It is concluded that there is no detectable interaction between hypochlorous acid and the ether. By purification of the hypochlorous acid, as described in the experimental section, it was found that only a 2% loss of titre in 4 hours was experienced in a mixture of aqueous anisic acid and hypochlorous acid at 25°. This behaviour supports the theory that hypochlorous acid reacts with the phenoxide ion. Anisole, phenetole, and anisic acid cannot form the phenoxide ion, and therefore do not react.

The behaviour of chlorine is significant. It can chlorinate the ether as well as the phenol, so that the chlorination of phenolic

* This velocity of formation of chlorine allows of the calculation of the speed of hydrolysis of chlorine, which is generally regarded as extremely rapid. The hydrolysis constant $[HOCl][H^{\cdot}][Cl']/[Cl_2]$ is $4{\cdot}84 \times 10^{-4}$ (Jakowkin, *loc. cit.*), and equals the ratio of the velocity coefficient of hydrolysis (k') to that of formation of chlorine by the reversible reaction (k)

$$HCl + HOCl \underset{k'}{\overset{k}{\rightleftharpoons}} Cl_2 + H_2O.$$

Thus $k'/k = 4{\cdot}84 \times 10^{-4}$, whence $k' = 1{\cdot}06 \times 10^{3}$. The speed of hydrolysis of chlorine is therefore relatively slow.

substances does not necessarily involve the phenoxide ion. This does not exclude the possibility of reaction between chlorine and the phenoxide ion in a solution of a phenol.

4. *Reactivity and Constitution.*

The velocity coefficients of chlorination by hypochlorite of a number of phenols have been measured at 25·0°, chiefly in alkaline solution because control of the hydroxyl-ion concentration is facilitated. The results are in Table VIII.

TABLE VIII.

	k_2.	K_a''.	$k_2 K_a''$.
Phenol	$3{\cdot}3 \times 10^{5}$	$1{\cdot}1 \times 10^{-10}$	$3{\cdot}63 \times 10^{-5}$
o-Cresol	$1{\cdot}25 \times 10^{6}$	$0{\cdot}63 \times 10^{-10}$	$7{\cdot}88 \times 10^{-5}$
m-Cresol	$4{\cdot}4 \times 10^{6}$	$0{\cdot}98 \times 10^{-10}$	$42{\cdot}00 \times 10^{-5}$
p-Cresol	$9{\cdot}0 \times 10^{5}$	$0{\cdot}67 \times 10^{-10}$	$6{\cdot}0 \times 10^{-5}$
o-Chlorophenol	$5{\cdot}9 \times 10^{4}$	$7{\cdot}7 \times 10^{-10}$	$4{\cdot}55 \times 10^{-5}$
p-Chlorophenol	$4{\cdot}90 \times 10^{4}$	$4{\cdot}1 \times 10^{-10}$	$2{\cdot}0 \times 10^{-5}$
3-Chloro-*p*-cresol	$1{\cdot}67 \times 10^{5}$		
o-Nitrophenol	$1{\cdot}01 \times 10^{3}$	$7{\cdot}5 \times 10^{-3}$	$7{\cdot}58 \times 10^{-5}$
m-Nitrophenol	$5{\cdot}89 \times 10^{3}$	$1{\cdot}0 \times 10^{-3}$	$5{\cdot}89 \times 10^{-5}$
p-Nitrophenol	$6{\cdot}84 \times 10^{2}$	$9{\cdot}6 \times 10^{-3}$	$6{\cdot}57 \times 10^{-5}$
1 : 3 : 4-Xylenol	$2{\cdot}02 \times 10^{6}$		

The velocity coefficients differ considerably from one another, but the products of the velocity coefficient and the ionisation constant of the phenols are grouped in a noteworthy manner about the value 7×10^{-5}. It appears that the reactivity of the phenoxide ion is proportional to its affinity for hydrogen ion. Those ions derived from phenols of high ionisation constant are least reactive. These results may be compared with those of Boyd and Thomas (J., 1919, **115**, 1239), who found a similar relation between the rates of interaction of phenoxide ions with olefine oxides.

5. *Discussion.*

1. Since the speed of interaction of a phenol and hypochlorous acid is proportional to the product of the concentrations of the un-ionised acid and the phenoxide ion, the halogenating agent cannot be the positive halogen ion, for its concentration is proportional to the hypohalous acid concentration divided by that of the hydroxyl ion, *i.e.*, $[Cl^{\cdot}] = K[HOCl]/[OH']$. The idea must also be abandoned in the case of chlorine, as its speed of chlorinating acetanilide, for example (Orton and King, J., 1911, **109**, 1369), is independent of the excess of chlorine ions present. It appears that the molecules of chlorine or of hypochlorous acid react as whole molecules, and that therefore an intermediate complex must exist as a transient stage of the reaction.

2. It is probable that the theory of the reactivity of the phenoxide ion which has been proved for the interaction of hypochlorous acid and phenols also applies to the similar reactions involving hypobromous and hypoiodous acids. The conclusion of Vortmann (*Ber.*, 1923, **56**, 234) that the alkali hypoiodite is the effective iodinating agent is based on evidence which also supports the mechanism involving the phenoxide ion. We find that the speed of iodination is decreased in strong alkaline solution, which can be explained by the great decrease in the concentration of the un-ionised hypoiodous acid.

3. Hypochlorous acid does not react with phenolic ethers, since they do not form the phenoxide ion, but chlorine interacts easily with both phenols and ethers. It is probable, however, that the interaction of chlorine with the phenol involves both the highly reactive phenoxide ion and the un-ionised phenol. Any alteration in the degree of ionisation of the phenol might be expected to alter the proportions of the isomeric products formed. Thus Arnall (J., 1924, **125**, 811) found that the proportions of *o*-, *m*-, and *p*-nitrophenols formed on nitration varied with the concentration of nitric acid present. This observation is consistent with the present theory of the reactivity of the phenoxide ion, the concentration of which varies with the acidity of the medium. The slower speed of bromination by bromine water in strong acid solution attributed by Francis (*loc. cit.*) to a decrease in the concentration of "nascent" bromine is also naturally explained on the present theory by the decrease in concentration of the phenoxide ion, the bromination of which is probably faster than that of the un-ionised molecule.

EXPERIMENTAL.

Method of Titration.—The course of a reaction was followed by estimation of the iodine liberated by the hypochlorous acid from acidified potassium iodide. The titration of iodine in the presence of a phenol must be carried out in acid solution in order to prevent interaction of the iodine and phenol. The consequent presence of free hydriodic acid, which is easily oxidised, is a source of error in the titration. The difficulty was overcome by using oxygen-free solutions and carrying out the titration in an atmosphere of nitrogen (compare Soper, J., 1924, **125**, 1899). Perfectly sharp end-points, with $N/500$-thiosulphate, were obtained in this way, even in the presence of $3N$-sulphuric acid.

Preparation and Purification of Hypochlorous Acid.—The hypochlorous acid was prepared by passing chlorine into water containing yellow mercuric oxide in suspension, or by distillation of a

bleaching powder solution through which carbon dioxide was passed. Both specimens of hypochlorous acid behaved in the same way after purification. Two methods of purification were used : (*a*) repeated distillation of the hypochlorous acid from yellow mercuric oxide under reduced pressure; (*b*) simply shaking the hypochlorous acid with yellow mercuric oxide and after some time filtering off the oxychloride. The latter method was the one finally adopted, since the distillation method gave a hypochlorous acid which, on addition of sulphuric acid, formed traces of chlorine, the presence of which was manifested by the greater rate of reaction with phenol.

Purity of Phenols.—Kahlbaum specimens were purified either by several crystallisations from suitable solvents or by distillation, preferably under reduced pressure. Two distillations were usually found sufficient tc give a pure phenol, the reactivity of which was unaltered by further distillation.

Water.—A high grade of conductivity water was used throughout. In such water a sample of hypochlorous acid showed no fall of titre in 60 hours.

Summary.

1. The interaction of phenols with hypochlorous acid in aqueous and in alkaline solution has been shown to involve the phenoxide ion and the un-ionised hypochlorous acid.

2. The reactivity of the ion with hypochlorous acid is least when the phenol from which it is derived is most strongly acidic. The reactivity of the ions of the simple phenols is roughly proportional to their affinity for hydrogen ions.

3. The chlorination of phenols and phenolic ethers by chlorine is a much faster reaction than the rate of formation of chlorine from a mixture of hydrochloric and hypochlorous acids, the velocity coefficient of which is $2{\cdot}2 \times 10^6$ at 25°. The calculated velocity coefficient of the hydrolysis of chlorine at this temperature is $1{\cdot}06 \times 10^3$.

4. The mechanism of halogenation of phenols is discussed.

In conclusion, we wish to acknowledge the helpful criticism of Professor K. J. P. Orton, F.R.S.

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CCVII.—*Compounds of Tervalent Molybdenum. Part IV. Bromides.*

By WILLIAM WARDLAW and ARTHUR JACOB IMMINS HARDING.

By electrolytic reduction of molybdenum trioxide dissolved in hydrochloric acid, solutions of tervalent molybdenum are obtained which, on addition of alkali chlorides, yield complex salts of the types $[MoCl_6]R_3$ and $[MoCl_5,H_2O]R_2$. Although the trichloride has not yet been isolated from such solutions, when the concentration of molybdenum is high, the oxychloride, $MoOCl,4H_2O$, can be obtained (J., 1924, **125**, 2370). From the reduced bromide solutions, Rosenheim and Braun (*Z. anorg. Chem.*, 1905, **46**, 311) have prepared two complex salts $[MoBr_6](C_5H_6N)_3$ and $[MoBr_5,H_2O](NH_4)_2$.

In all these cases, the co-ordination number is 6. Moreover, the different halogen complexes containing molybdenum in other stages of oxidation exhibit this co-ordination number, for in such compounds an oxygen atom occupies only one co-ordination position: *e.g.*, $[MoO_2Cl_4]R_2$, $[MoO_2Br_4](C_5H_6N)_3$, $[MoOX_5]R_2$ where X = Cl, Br, or F.

On the Bohr theory of atomic structure, molybdenum, like chromium, iron, cobalt, nickel, rhodium, osmium and platinum, which all form well-defined compounds of co-ordination number 6, is a member of one of the groups of elements the planetary electrons of which are undergoing reorganisation. It shows, therefore, variable valency and marked colour in its compounds. The *maximum* co-ordination number of molybdenum is not, however, 6. A co-ordination number of 8 is seen in the complex salt $R_4Mo(CN)_8$. This is in accordance with Sidgwick's rule that the maximum co-valency number or co-ordination number is that of the maximum sub-group next to the largest completed group in the atom. Molybdenum, atomic number 42, has its 3-quanta orbits completed and the numbers of electrons in the 4-quanta sub-groups are 2, 2, 4, 4, 6, 6, 8. So far, 6 represents the maximum co-ordination number for tervalent molybdenum and further evidence for this is afforded by the results of the present investigation, whereby, from a reduced solution of molybdenum trioxide in hydrobromic acid, a fawn-coloured oxybromide $[MoOBr,4H_2O]$ and red salts of the general formulæ $R_3[MoBr_6]$ and $R_2[MoBr_5,H_2O]$ have been isolated.

EXPERIMENTAL.

Molybdenyl Monobromide.—The most satisfactory method for the preparation of constant-boiling hydrobromic acid is that outlined

by Scott (J., 1900, **77**, 648), in which bromine is covered with water and reduced by sulphur dioxide and the resulting homogeneous liquid is distilled, the fraction boiling at 124—126° being collected and re-distilled.

In preparing his electrolyte, Rosenheim (*loc. cit.*) dissolved the dihydrate of molybdenum trioxide in the hydrobromic acid. However, the trioxide itself will dissolve in the hot acid. 25 G. of molybdenum trioxide and 350 c.c. of the hydrobromic acid were heated under reflux for 3 to 6 hours, the final solution being golden-brown in colour. The filtered solution was electrolysed in a diaphragm cell with smooth platinum electrodes (J., 1923, **123**, 169), a current of 3·5 amps. being used, until the cathode solution was reddish-brown. This solution was transferred to an air-free flask and concentrated at 70° under diminished pressure to 80—100 c.c. The liquid was then transferred to a small cell and re-electrolysed to ensure that the molybdenum was tervalent. The electrolysis was continued until a sample of the liquid added to air-free acetone gave a flocculent fawn precipitate of molybdenyl bromide. (If the electrolysis is continued beyond this stage, the product is hydrolysed and much darker than the true compound.) The cathode solution was now forced by pressure of carbon dioxide into air-free acetone, and the solid which separated was filtered off and washed with acetone. All these operations were performed in an atmosphere of carbon dioxide, air being rigidly excluded. The solid was transferred to a desiccator which was then evacuated.

Valency of the Compound.—This was determined as for the oxychloride (*loc. cit.*). Direct titration with standard permanganate required, for 1 g. of solid, 118·90 c.c. After oxidation and passage through the reductor a solution containing 1 g. of the substance required 118·40 c.c. The molybdenum is therefore tervalent, for the latter titration represents the oxidation of the tervalent molybdenum, produced by reduction, to the sexavalent condition.

Analysis.—The molybdenum was precipitated as sulphide and ignited to trioxide (J., 1924, **125**, 1911). The bromide in the filtrate and washings was weighed as silver bromide (Found: Mo, 37·5, 37·7; Br, 31·1, 31·3; Mo : Br = 1 : 1; 1 : 1. $MoOBr,3{\cdot}5H_2O$ requires Mo, 37·7; Br, 31·35%). In all probability the normal hydrate is $MoOBr,4H_2O$.

Properties and Reactions of Molybdenyl Monobromide.

The dried solid is light fawn in colour and does not deliquesce in the air, although it gradually undergoes atmospheric oxidation. It is readily soluble in water or hydrobromic acid, its solubility in water being greater than that of the oxychloride. It is insoluble

in acetone or dry ether, slightly soluble in cold absolute alcohol and more soluble on warming. The substance has pronounced reducing properties. Silver nitrate is reduced to the metal, whilst with lead acetate acidified with acetic acid no precipitate of lead bromide is obtained. This test seems to indicate that molybdenyl bromide is not a binary electrolyte.

Molecular Weight Determinations.—The molecular weight was determined by depression of the freezing point of air-free water.

G. of $MoOBr,4H_2O$ per 10 g. of water ...	0·1235	0·0640	0·0698
" Apparent " mol. wt.	218·8	218·2	220·1

If the salt has the formula $[MoOBr,4H_2O]$, the molecular weight is 263·9, whereas if it is formulated as $[MoO]Br,4H_2O$ in dilute aqueous solution, if ionisation is complete, its " apparent " molecular weight should be 131·9. The above results furnish strong evidence in favour of its formulation as the co-ordination compound $[MoOBr,4H_2O]$, although they also indicate that the substance undergoes gradual hydrolysis in accordance with the equation

$$[MoOBr,4H_2O] + H_2O = [MoO,5H_2O]Br = [MoO,5H_2O]^{\cdot} + Br'.$$

This view receives support from the fact that the molecular weights determined with solutions of the solid, after standing some hours in ice-cold water, were considerably less than those quoted above, whilst after longer periods the hydroxide of molybdenum gradually separated.

Conductivity measurements at 1° showed this continuous hydrolysis, which was accelerated by the presence of the electrodes (compare Duff, J., 1923, **123**, 572). For $v = 24$ litres per mole

μ	66·8	68·2	75·2	76·1	76·9	77·6	77·8	78·2	78·2
Time (mins.) ...	2	3	4	5	6	7	8	9	10

In more dilute solutions, the rate of hydrolysis was increased. The fact that the conductivity alters with time and that it approaches the value for a binary electrolyte like potassium chloride, for which the data at 1° are

v (litres per mole)	8	16	32
μ	72·2	75·2	77·3

supports the formula $[MoOBr,4H_2O]$ for the new compound. Many cases could be cited to show that ionisation of co-ordination compounds occurs with replacement of the co-ordinated halogen atom by a molecule of the solvent.

Salts of the Types $R_3[MoBr_6]$ *and* $R_2[MoBr_5,H_2O]$.

By the addition of alkali bromide to a reduced bromide solution containing tervalent molybdenum, two salts have so far been pre-

pared conforming to the above types. The isolation of the oxybromide from a reduced molybdenum solution shows that a further possibility of complex salt formation may arise, namely, salts of the type $MoOBr,x$KBr. Although such a salt has not been isolated, the corresponding chlorine derivative $[MoOCl_2,3H_2O]K$ has been obtained (unpublished research). The preparation of these three classes of salts depends on the following factors: (*a*) Molybdenum concentration, (*b*) relative amount of alkali bromide present, (*c*) amount of "free" acid. By suitable adjustment of these factors we have isolated K_3MoBr_6, K_2MoBr_5, Cs_2MoBr_5,H_2O, and an impure rubidium salt of the last type.

Preparation of Tripotassium Molybdenum Hexabromide.—200 C.c. of the bromide solution containing tervalent molybdenum, to which was added a saturated aqueous solution of 10 g. of potassium bromide, were concentrated at 65—70° under diminished pressure to about 100 c.c. Air-free alcohol was then admitted to the flask, and the excess of potassium bromide precipitated. After filtration in an atmosphere of carbon dioxide, the filtrate was concentrated to 40 c.c. On addition of absolute alcohol a crystalline, light red solid was obtained which was filtered off and dried (Found: Mo, 13·9; Br, 69·0; K, 16·9. K_3MoBr_6 requires Mo, 13·9; Br, 69·2; K, 16·9%). A valency determination showed the molybdenum in this salt to be tervalent.

Preparation of Dipotassium Molybdenum Pentabromide.—100 C.c. of the solution containing tervalent molybdenum and 20 c.c. of potassium bromide solution (containing 1·5 g.) were placed in an air-free flask and concentrated at 65—70° under diminished pressure until nearly dry. At this stage, air-free alcohol was admitted and a crystalline, brick-red salt separated which, after filtration and drying in an evacuated desiccator, was shown to contain tervalent molybdenum (Found: Mo, 16·7; Br, 69·5; K, 13·8. K_2MoBr_5 requires Mo, 16·7; Br, 69·6; K, 13·6%).

This salt is obviously of the same type as the ammonium salt first obtained by Rosenheim and Braun (*loc. cit.*) and later by Foerster and Fricke (*Z. angew. Chem.*, 1921, **36**, 2, 458). The former investigators formulated the dark garnet-red crystals as $(NH_4)_2MoBr_5,2H_2O$, whilst Foerster and Fricke considered them to be $(NH_4)_2[MoBr_5,H_2O]$. By double decomposition with cæsium bromide a solution of the potassium salt yielded the very insoluble Cs_2MoBr_5,H_2O (Found: Mo, 12·3; Mo : Br = 1 : 5. Calc.: Mo, 12·3%).

A rubidium salt was prepared by a similar method to that used for the potassium derivative, but it could not be obtained pure.

Properties of the Complex Salts.

All these soluble complex salts give deep red solutions with water, in which both potassium salts are very soluble, the rubidium salt is sparingly soluble, and the cæsium compound insoluble. The aqueous solutions gradually turn brown, then turbid, and finally yield a dark brown precipitate. This decomposition is accelerated by warming. The salts reduce copper sulphate solution to cuprous bromide, whilst silver nitrate solution is reduced to the metal.

The authors desire to thank Messrs. Brunner Mond and Co. for a grant in aid of this investigation and Professor G. T. Morgan, F.R.S., for his continuous interest.

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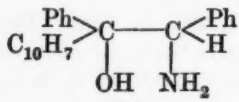
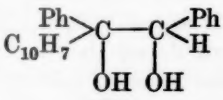
CCVIII.—*The Dehydration of Glycols derived from α-Naphthylglycollic Acid.*

By ALEX. McKENZIE and WALTER SAMUEL DENNLER.

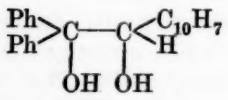
THE present investigation arose from previous work on the deamination of 2-hydroxy-1 : 2-diphenyl-2-α-naphthylethylamine (I) and on the dehydration of α-naphthylhydrobenzoin (II) (McKenzie and Richardson, J., 1923, **123**, 79; McKenzie and Roger, J., 1924, **125**, 844; McKenzie and Dennler, *ibid.*, p. 2105; Tiffeneau and Orékhov, *Compt. rend.*, 1924, **178**, 1619). It appeared likely that 1-α-*naphthyl*-2 : 2-*diphenylethylene glycol* (III), which is isomeric with (II), would behave very differently when acted on by sulphuric acid. By arrangement with Professor Tiffeneau, it is now shown in the present paper that this is the case.



(I.)



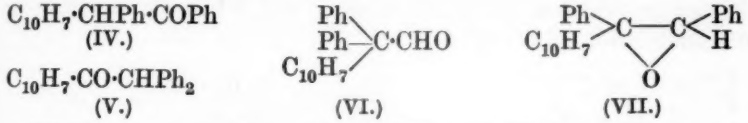
(II.)



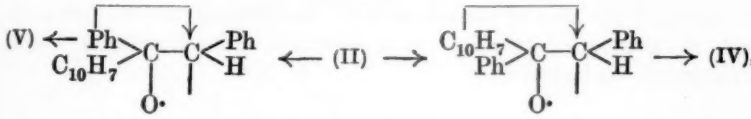
(III.)

The products resulting from the elimination of water from (II) have already been shown to depend on the experimental conditions. With cold concentrated sulphuric acid, both α-naphthyldeoxybenzoin (IV) and diphenylacetonaphthone (V) were formed, whereas with hot dilute sulphuric acid the products were α-naphthyldeoxybenzoin

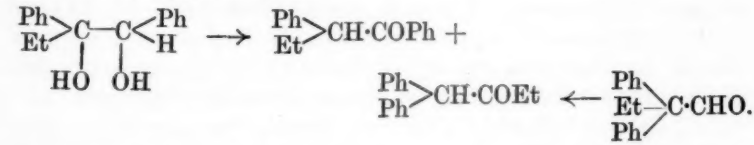
(IV), diphenyl-α-naphthylacetaldehyde (VI), and diphenyl-α-naphthylethylene oxide (VII).



Whilst the formation of both (IV) and (V) from (II) may be interpreted on the basis of semipinacolinic transposition,



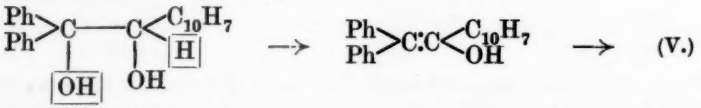
it should be noted that Danilov (*J. Russ. Phys. Chem. Soc.*, 1919, **51**, 97) has shown that triphenylacetaldehyde undergoes molecular rearrangement into phenyldeoxybenzoin even under the influence of hot dilute sulphuric acid, thus: CPh_3·CHO → $CHPh_2$·COPh. Similarly, Orékhov and Tiffeneau (*Compt. rend.*, 1926, **182**, 67) have shown that substituted acetaldehydes undergo transformation into the same ketones as are formed by the direct dehydration of the corresponding glycols, *e.g.*, a mixture of ethyldeoxybenzoin and diphenylbutanone is obtained either from diphenylethylacetaldehyde or from ethylhydrobenzoin:



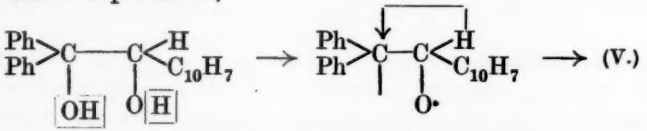
In the light of these results, it would appear quite probable that, in the formation of (IV) and (V) from (II), the intermediate product might be (VI). The proportion of (IV) and (V) in the mixture resulting from the dehydration of (II) with cold concentrated sulphuric acid varies according to the experimental conditions, and it might not be easy to arrive at this proportion experimentally, more particularly since the ketones melt at practically the same temperature. The recent work of Luce (*Compt. rend.*, 1925, **180**, 145), however, would indicate that the migrational aptitude of α-naphthyl is greater than that of phenyl, and one would argue that, in the mixture of ketones referred to, (IV) should preponderate.

1-α-Naphthyl-2 : 2-diphenylethylene glycol was prepared by the action of magnesium phenyl bromide on methyl α-naphthylglycollate. It gave the same ketone, namely, diphenylacetonaphthone (V), irrespective as to whether cold concentrated sulphuric acid or hot

dilute sulphuric acid was used as the dehydrating agent, and its behaviour is thus quite different from that of the isomeric glycol (II). The change, which is best depicted as a vinyl dehydration, involves no transposition of phenyl:



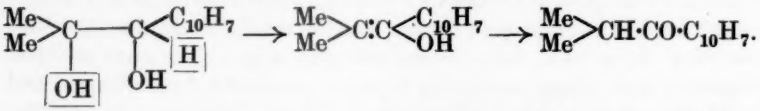
Since phenyl has undoubtedly a stronger saturation capacity than α-naphthyl, the sum of the saturation capacities of the two phenyls will be greater than that of α-naphthyl plus hydrogen. The alternative explanation,



which involves migration of hydrogen in preference to α-naphthyl, is regarded as unsatisfactory.

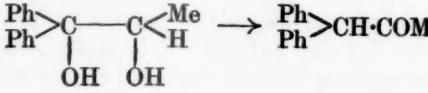
The researches of both Meerwein and Tiffeneau have demonstrated that phenyl has a strong saturation capacity, and a comparison of the results obtained by dehydrating (II) and (III) will show that the saturation capacity of phenyl is greater than that of α-naphthyl. Obviously, the dehydration of (III) is not a semipinacolinic change; if it were, the product would be (IV) and not (V). Of the two hydroxyls, the tertiary is the more loosely bound, because the saturation capacity of the two phenyl groups more than balances the saturation capacity of α-naphthyl plus hydrogen.

1-α-*Naphthyl*-2 : 2-*dimethylethylene glycol* was prepared from methyl α-naphthylglycollate and magnesium methyl iodide. Its behaviour on dehydration is similar to that of (III):

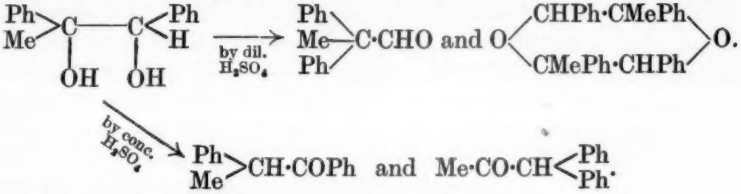


This result was anticipated, since methyl has a strong saturation capacity.

The behaviour of (III) and (II) on dehydration has a parallel in two other cases which may be quoted. Thus, diphenylpropylene glycol gives diphenylacetone both with hot dilute and with cold concentrated sulphuric acid:

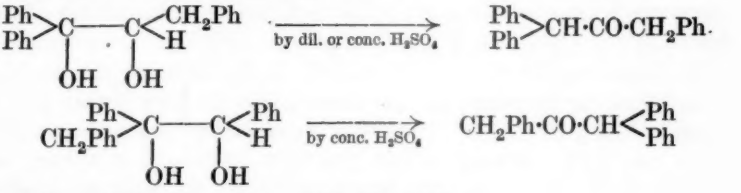


The isomeric methylhydrobenzoin, however, behaves differently :



(For literature, see McKenzie and Roger, *loc. cit.*)

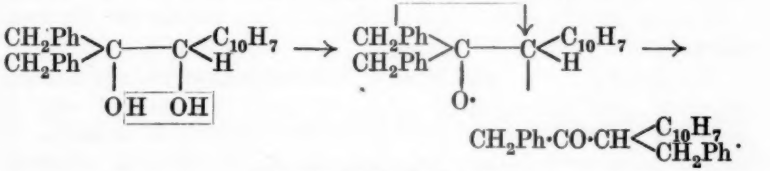
Again, *as*-benzyldiphenylethylene glycol may be contrasted with the isomeric benzylhydrobenzoin :



(Orékhov, *Bull. Soc. chim.*, 1919, **25**, 107).

Here the same ketone is produced by two different mechanisms, migration of phenyl taking place in the one case and not in the other.

The ketones formed from 1-α-naphthyl-2 : 2-diphenylethylene glycol and 1-α-naphthyl-2 : 2-dimethylethylene glycol, respectively, cannot exist in optically active modifications. To obtain such a ketone from a glycol derived from optically active α-naphthylglycollic acid, it would be necessary for semipinacolinic change to occur during the dehydration of the glycol instead of the vinyl dehydration as in the two other cases, and even then optical activity might not persist. Accordingly, since Tiffeneau and Lévy (*Bull. Soc. chim.*, 1923, **33**, 759) have shown that benzyl has a greater migrational aptitude than methyl and also has a weaker saturation capacity, the examination of the dehydration of 1-*α-naphthyl*-2 : 2-*dibenzylethylene glycol* (VIII), prepared by the action of magnesium benzyl chloride on methyl α-naphthylglycollate, was undertaken. The change is apparently semipinacolinic :



EXPERIMENTAL.

Preparation of α-Naphthylglycollic Acid.—(1) *From α-naphthoic acid.* Boessneck's method (*Ber.*, 1883, **16**, 639) was modified as

follows: α-Naphthoic acid (40 g.) → acid chloride (37 g.), b. p. 170—172°/15 mm., → α-naphthoyl cyanide (27 g.), m. p. 100°, → α-naphthoylformamide (24 g.), m. p. 151—153°, → α-naphthoylformic acid (15 g.), m. p. 110—111°. The latter acid was reduced by aluminium turnings and an excess of caustic potash, the excess of aluminium removed, and the hydroxy-acid obtained by acidification by hydrochloric acid and extraction with ether. It crystallised from benzene in rectangular needles, m. p. 80—82°, and was then dried in a vacuum. Yield: 14 g.; m. p. 98·5—99·5° (Found: C, 71·2; H, 5·0. Calc.: C, 71·3; H, 5·0%). Boessneck does not quote the melting point of his acid, but Brandis (*Ber.*, 1889, **22**, 2148), who obtained the acid from α-naphthaldehyde by the cyanohydrin method, gives m. p. 80—81°.

(2) *From naphthalene.* α-Naphthyl methyl ketone (14 g.), prepared from naphthalene by the Friedel and Crafts reaction (Caille, *Compt. rend.*, 1911, **153**, 393), was brominated (Schweitzer, *Ber.*, 1891, **24**, 549). Caustic potash (25 g. in 250 c.c. of water) was added to the dibromide and, after a fortnight, the acid obtained by acidification and extraction with ether was crystallised from benzene (yield of dry acid, 5 g.; m. p. 98—99°. Schweitzer gives m. p. 91—93°).

(3) *From chloral* (compare Hébert, *Bull. Soc. chim.*, 1920, **27**, 45). The Grignard reagent prepared from 150 g. of α-bromonaphthalene (1 mol.) was cooled to −12°, and an ethereal solution of 98 g. of anhydrous chloral (1 mol.) gradually added (90 min.). The action was very vigorous, the ether assumed a blood-red tint, and a solid separated. The mixture remained at 0° over-night, and was then decomposed by ice and dilute acetic acid. The oil resulting from the ethereal solution was mixed with an excess of sodium carbonate, and, after hydrolysis of the trichloro-alcohol and removal of the naphthalene by steam, the aqueous solution was acidified by concentrated hydrochloric acid, and the hydroxy-acid extracted with ether (yield: 70 g.). The acid after crystallisation from benzene and drying in a vacuum melted at 98—99°. Its *silver* salt gave Ag, 35·0 (Calc.: Ag, 35·0%).

Of those three methods, the third was in our experience the most practicable.

α-Naphthylglycollic acid gives a blue coloration when a trace is added to cold concentrated sulphuric acid. Its methyl ester is sparingly soluble in light petroleum, from which it separates in needles, m. p. 79°, as given by Schweitzer (*loc. cit.*) (Found: C, 72·2; H, 5·6. Calc.: C, 72·2; H, 5·6%). When heated under pressure at 100° with aqueous ammonia (*d* 0·88), the ester was converted into *α-naphthylglycollamide*, $C_{10}H_7 \cdot CH(OH) \cdot CO \cdot NH_2$, which crystallises

from acetone–light petroleum in rhombic plates, m. p. 134—135° (Found: C, 71·8; H, 5·7. $C_{12}H_{11}O_2N$ requires C, 71·7; H, 5·5%). An attempt to prepare the ketol, $C_{10}H_7 \cdot CH(OH) \cdot CO \cdot C_6H_5$, by the action of an excess of magnesium phenyl bromide on the acid amide led to the regeneration of the latter.

Action of Grignard Reagents on Methyl α-Naphthylglycollate.

Action of Magnesium Phenyl Bromide.—An ethereal solution of 5 g. of the ester (1 mol.) was added during 45 minutes to the Grignard reagent prepared from 16 g. of bromobenzene (4½ mols.). A solid separated during the heating (9 hours). The product was decomposed with ice and ammonium chloride and, after the usual manipulation, diphenyl was removed by light petroleum. The 1-*α-naphthyl*-2 : 2-*diphenylethylene glycol* (III) obtained crystallised from light petroleum (b. p. 60—100°), in which it was sparingly soluble, in rectangular needles, m. p. 126—127° (yield 6·1 g.). It gives a bright green coloration with concentrated sulphuric acid. For analysis, it was dried in a vacuum at 80° (Found: C, 84·6; H, 6·0. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%).

Action of Magnesium Methyl Iodide.—The conditions were similar to the preceding (15 g. of the ester [1 mol.]; Grignard reagent prepared from 60 g. of methyl iodide [6 mols.]; decomposition with ice, ammonium chloride and ammonia). The crude product was crystallised twice from light petroleum, 1-*α-naphthyl*-2 : 2-*dimethylethylene glycol*, $C_{10}H_7 \cdot CH(OH) \cdot CMe_2 \cdot OH$, being obtained (11 g.) in clumps of rectangular prisms, m. p. 81·5—82° (Found: C, 78·0; H, 7·5. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·5%). It gives a reddish-brown coloration with concentrated sulphuric acid.

Action of Magnesium Benzyl Chloride.—An ethereal solution of 14 g. of the ester (1 mol.) was added during 90 minutes to the Grignard reagent prepared from 40 g. of benzyl chloride (4½ mols.). A solid separated during the heating (10 hours). The product was decomposed with ice and dilute sulphuric acid, and dibenzyl removed by light petroleum. The 1-*α-naphthyl*-2 : 2-*dibenzylethylene glycol* (VIII) obtained crystallised from rectified spirit in rectangular plates (17 g.), m. p. 174—175° (Found: C, 84·8; H, 6·7. $C_{26}H_{24}O_2$ requires C, 84·8; H, 6·6%). It gives a purple coloration with concentrated sulphuric acid.

Dehydration of Glycols derived from Methyl α-Naphthylglycollate.

Dehydration of the Diphenyl Glycol.—(a) *With concentrated sulphuric acid.* 2 G. of finely-powdered 1-α-naphthyl-2 : 2-diphenylethylene glycol were triturated in instalments with 30 c.c. of concentrated sulphuric acid during 2 hours. The bright green color-

ation which appeared at first changed gradually to a greenish-brown. The mixture was added to 100 g. of ice, and the ethereal extract dried with sodium sulphate. The resulting oil gradually solidified, and the solid crystallised from rectified spirit in glistening rhombic plates, m. p. 108—109°. The compound (0·9 g.) was identified as diphenylacetonaphthone by its colour reaction with concentrated sulphuric acid, and by the non-depression of melting point when mixed with a specimen of the ketone prepared by the dehydration of α-naphthylhydrobenzoin with concentrated sulphuric acid (McKenzie and Roger, *loc. cit.*).

(b) *With dilute sulphuric acid.* A mixture of the glycol (2 g.), water (16 c.c.), and concentrated sulphuric acid (20 g.) was boiled for 2 hours under reflux. The mixture was cooled, diluted with water, and the oil extracted with ether. The product was crystallised from ethyl alcohol, and diphenylacetonaphthone (1·5 g.), identified as above, was isolated.

Dehydration of the Dimethyl Glycol.—(a) *With concentrated sulphuric acid.* 7 G. of 1-α-naphthyl-2 : 2-dimethylethylene glycol were dehydrated with 100 c.c. of concentrated sulphuric acid. 2 G. of a golden-yellow oil, b. p. 295—298°, were collected.

(b) *With dilute sulphuric acid.* 10 G. of the glycol were boiled for 2½ hours with a mixture of 100 g. of concentrated sulphuric acid and 100 c.c. of water. The resulting oil was fractionated, and the portion boiling at 304—306°/758 mm. was collected. It did not reduce Fehling's solution, nor did it restore the colour to Schiff's reagent. Yield 6 g. (Found : C, 85·3; H, 7·0. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·1%). This was *iso*propyl α-naphthyl ketone, which according to Rousset (*Bull. Soc. chim.*, 1896, **15**, 66) has b. p. 308—310°. The scission of the oil with alcoholic potash gave a solution of potassium salt from which α-naphthoic acid was isolated, and the oil from the dehydration with concentrated sulphuric acid underwent a similar decomposition.

Dehydration of the Dibenzyl Glycol.—(a) *With concentrated sulphuric acid.* 10 G. of 1-α-naphthyl-2 : 2-dibenzylethylene glycol were gradually added (1 hour) with constant trituration to 220 g. of concentrated sulphuric acid. A purple coloration was noted. After being kept for 2 hours at the ordinary temperature, the mixture was poured into 500 g. of ice; the purple coloration then disappeared and the temperature fell quickly to −2°. When the ice had melted, the oil was extracted with ether, the ether expelled, and the residue (7 g.) distilled under diminished pressure. The *compound*, $C_{26}H_{22}O$, was a golden-yellow oil, b. p. 275°/15 mm. For analysis, it was dried in a vacuum (Found : C, 89·3; H, 6·3. $C_{26}H_{22}O$ requires C, 89·2; H, 6·2%). It solidified after several days,

and was then crystallised from rectified spirit, from which it separated in rhombic plates, m. p. 58—59°. With concentrated sulphuric acid, it gave a light brown coloration which disappeared quickly.

(b) *With dilute sulphuric acid.* A mixture of the glycol (15 g.), water (125 c.c.), and concentrated sulphuric acid (120 g.) was boiled for about 2½ hours under reflux, and the oil extracted with ether. The product was an oil (13·5 g.), b. p. 276°/15 mm., which gradually solidified; m. p. 58—59°.

The substance is probably benzyl-α-naphthylmethyl benzyl ketone, $CH_2Ph{\cdot}CO{\cdot}CH(C_{10}H_7){\cdot}CH_2Ph$, but the evidence for its constitution is not quite convincing. It formed no oxime with hydroxylamine, and it is very stable towards alcoholic soda; thus, when 2·5 g. were heated at 100—140° for 24 hours with a solution of 6 g. of caustic soda in ethyl alcohol, the original substance was recovered. It gave, however, benzoic acid when it was oxidised in glacial acetic acid solution with chromic anhydride. The first product of the oxidation was presumably phenylacetic acid; it was found that the latter does give benzoic acid when oxidised under similar conditions to those adopted for the compound.

The thanks of the authors are due to the Department of Scientific and Industrial Research for a maintenance grant awarded to one of them (W. S. D.).

UNIVERSITY COLLEGE, DUNDEE.
UNIVERSITY OF ST. ANDREWS. [*Received, February 20th,* 1926.]

CCIX.—*The Complexity of the Solid State. Part IV. The Behaviour of Pure Sulphur Trioxide. Part III.*

By ANDREAS SMITS and PIETER SCHOENMAKER.

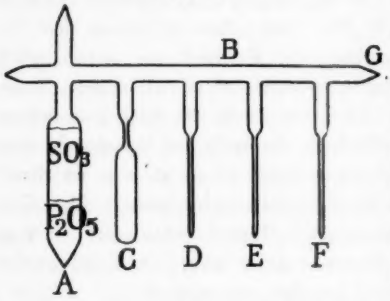
Investigations with X-Rays.

As shown in our last publication (this vol., p. 1120), it is possible by partial distillation to obtain the intensively dried, high-melting, asbestos-like form in a condition having an abnormally low vapour pressure and an initial melting point which is 33° higher than the unary melting point. It appears, indeed, that this form of sulphur trioxide behaves as a mixed crystal; the most volatile pseudo-component can be distilled off, so that the residue is a substance having the above abnormal properties.*

* Only the states of aggregation of a single substance in inner equilibrium will be called "modifications"; the states not in inner equilibrium will be termed "forms" of the substance.

For the *X*-ray investigation of the different states of the high-melting, asbestos-like form we used the simple apparatus of high-melting Jena glass shown in Fig. 1. The bulb, A, is sealed to B along with a vessel, C, and three very thin-walled capillary tubes, D, E, and F (diameter 0·008 to 0·01 mm.). Bulb A is partly filled with freshly-distilled phosphorus pentoxide and then with intensively dried sulphur trioxide, as described in our first communication (J., 1924, **125**, 2557). The apparatus is then evacuated and the tube B is sealed off at G.

FIG. 1.



The capillary tubes were filled one after another with the high-melting, asbestos-like form by the method of condensation and evaporation. In order to obtain a form with an abnormally low vapour pressure, a part of the contents was distilled off rapidly and the capillaries were subsequently sealed off.

The Röntgenogram was then taken, using CuK_α-rays. We obtained a film of 15 lines, the strongest of which are given in the following table :

Distances (mm.)	8·9	11·6	13·2	16·4
$10^3 \times \sin^2\theta/2$	32	54	70	106

(θ is the angle between the incident and refracted beams; the intensities of the lines mentioned here were very strong.)

The same capillary was now heated at 50° for 48 hours and, since our experiments had shown that under these conditions the low vapour pressure of the high-melting, asbestos-like form (which had been disturbed by evaporation) increased strongly, it was expected that the Röntgenogram taken after this heating process would show a great difference. *It was, however, unchanged. Hence, either the X-ray method was unable to detect the change which had taken place in the solid, or the X-rays had already effected the establishment of the inner equilibrium during the first exposure, so that the state of the solid before and after the heating was in reality the same.*

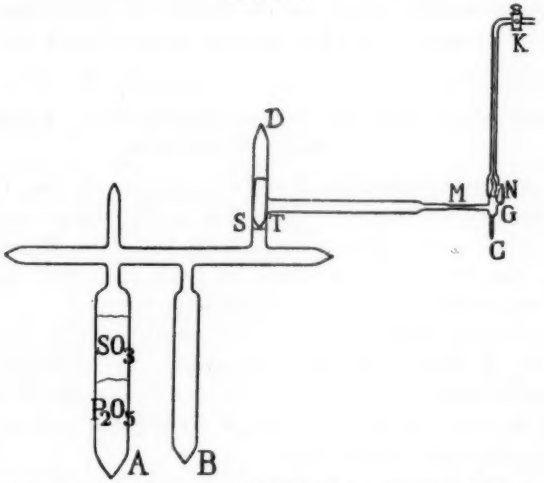
X-Rays effect the Establishment of the Inner Equilibrium.

To decide between the alternatives mentioned above, the following apparatus (Fig. 2) was constructed. As in other cases, pure phosphorus pentoxide was first distilled into vessel A, and then intensively dried sulphur trioxide. A T-piece with septum S was then connected with an exceedingly small glass spring indicator,

G, the little vessel of which was provided with a very thin-walled capillary, C, as used in *X*-ray analysis. The storage apparatus containing the sulphur trioxide was first evacuated and sealed; then the glass spring indicator with its capillary and the T-piece with its breaker were heated to redness in a current of dried air, the breaker-tube was sealed off at D, and this part of the apparatus was evacuated by stopcock K.

Capillary N being sealed off, a part of the sulphur trioxide was distilled into B and this vessel also was sealed off. Septum S was then broken and the capillary C filled with the high-melting, asbestos-like form, by the method of alternate condensation and evaporation.

FIG. 2.



In order to get a highly-disturbed state of this form, a portion was distilled off in the way described above, and then the capillary M was sealed off. The vapour pressure at the ordinary temperature was only 1 cm. Hg, proving that we had indeed a strongly-disturbed state of the high-melting, asbestos-like form.

We now placed the apparatus in front of our *X*-ray tube, protecting it by asbestos plates from access of heat. The *X*-rays were allowed to penetrate only the capillary containing the sulphur trioxide. As soon as this capillary was exposed to the *X*-rays the pressure in the indicator began to rise, showing that *X*-rays rapidly effect a transformation in the direction of inner equilibrium. In order to determine the final pressure, observations were continued over a period with the following results:

Time of exposure (hrs.)	0	1	4	8	10	13
Vapour pressure (mm. Hg) ...	10·8	22·2	43·1	46·1	46·3	46·3
Temperature	18·0°	18·0°	18·0°	18·8°	19·7°	19·7°

Consequently the final vapour pressure is 46·3 mm. Hg at 19·7°. As shown previously (this vol., p. 1116), the vapour-pressure line for the high-melting, asbestos-like form in inner equilibrium is given by the equation $T\ln P = -Q/R + CT$, where $C = 32{\cdot}0$. Now, giving Q/R the mean, *i.e.*, 8243 cals., of the three values obtained (8246, 8236 and 8246 cals.), we find, for $T = 292{\cdot}7°$ (*i.e.*, 19·7° C.), $P = 46{\cdot}45$ mm. Hg.

The agreement of this figure with the final value shown in the foregoing table proves that *X*-rays do indeed effect the establishment of inner equilibrium. It appears, therefore, that the *X*-ray diagrams showed no difference because, on exposure to *X*-rays, the substance was transformed into the state of inner equilibrium. This very interesting result shows that it is impossible to study the disturbed states of sulphur trioxide more closely by means of *X*-rays.

X-Rays bring about the Transformation of the Metastable into the Stable Modification.

Finally we investigated the *X*-ray diagrams of the two metastable modifications of sulphur trioxide—the ice-like form and the low-melting, asbestos-like form. Not only were the films obtained identical, but the *X*-ray diagram in each case was that of the high-melting, asbestos-like form considered above.

Hence *X*-rays, besides effecting the establishment of the inner equilibrium of sulphur trioxide, transform the metastable states into the stable state, *i.e.*, the high-melting, asbestos-like modification. *The only X-ray diagram obtainable is accordingly that of the stable modification in inner equilibrium.*

Summary.

On distillation of a portion of the intensively dried, high-melting, asbestos-like form, different states having abnormally low vapour pressures and abnormally high initial melting points were obtained, thus showing that the intensively dried, high-melting, asbestos-like form behaves as a mixture of pseudo-components which have very different vapour pressures and melting points.

At the ordinary temperature these states do not alter, but at 50° changes take place in the direction of the inner equilibrium. On studying the unchanged state and that changed at 50°, by means of *X*-rays, a very interesting result was obtained: the Röntgenograms in these two cases were identical.

Using an apparatus which enabled us to determine the vapour pressure during the exposure to *X*-rays, we found the explanation of the interesting phenomenon mentioned above to lie in the fact

that the *X*-rays effect a very rapid increase of the vapour pressure, proving that *X*-rays cause a rapid change in the direction of the inner equilibrium. Calculation showed that the final vapour pressure was exactly that of the high-melting, asbestos-like form in inner equilibrium.

X-Rays bring about not only the establishment of the inner equilibrium, but also the transformation of the metastable modifications into the stable form. The films obtained by exposing the ice-like form and the low-melting, asbestos-like form to *X*-rays are thus identical with the film of the high-melting, asbestos-like modification.

THE UNIVERSITY, AMSTERDAM. [*Received, March 8th*, 1926.]

CCX.—*The Photolysis of Acetaldehyde and of Acetone.*

By EDMUND JOHN BOWEN and HAROLD GARFIT WATTS.

IT was shown by Berthelot and Gaudechon (*Compt. rend.*, 1913, **156**, 68, 233) that acetaldehyde is partly polymerised in ultra-violet light and partly decomposed into methane and carbon monoxide; also (*ibid.*, 1910, **151**, 478) that acetone is decomposed into ethane and carbon monoxide. In aqueous solutions acetone is said to be photolysed to methane and acetic acid.

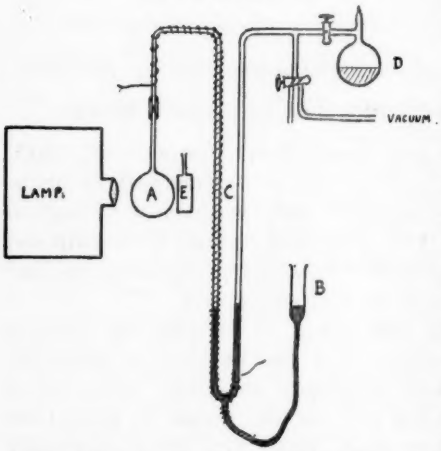
The following experiments were made to compare the number of molecules chemically changed with the number of molecules activated, *i.e.*, with the number of quanta absorbed. No work of this kind on gaseous aldehydes and ketones seems to have been done, although Volmar (*Compt. rend.*, 1924, **178**, 697), apparently without experimental evidence, assumed that these reactions obeyed the Einstein-Stark law.

Experiments with Acetaldehyde Vapour.

The apparatus is shown diagrammatically in the figure. A mercury vapour lamp made by the Thermal Syndicate was contained in a box fitted with quartz condensing lenses so that approximately parallel light fell on the fused quartz reaction bulb A, which was filled with acetaldehyde vapour by lowering the mercury reservoir B, evacuating with two mercury vapour pumps in series, and then connecting with the liquid aldehyde in D through the tap. The reservoir B was then raised so that mercury rose in the limbs of the U-tube C, and the tap on the right hand limb opened to the atmosphere. The amount of photochemical change was measured by pressure changes in the left hand limb, which was heated electrically to prevent condensation of liquid.

For the measurement of the energy of the ultra-violet light, use was made of the "ultra-violet radiometer" of Anderson and Robinson (*J. Amer. Chem. Soc.*, 1925, **47**, 718) which is based upon the decomposition of oxalic acid in uranyl sulphate solutions. There is a serious discrepancy in the results of different investigators of this reaction. Anderson and Robinson state that in ultra-violet light 1 molecule of oxalic acid is decomposed for every 25 quanta absorbed; Boll (*Compt. rend.*, 1913, **156**, 1891) states that 50 molecules of oxalic acid are decomposed for each quantum absorbed; whilst Büchi (*Z. physikal. Chem.*, 1924, **111**, 269) finds that the reaction obeys the Einstein-Stark law. We therefore made direct measurements of the photochemical efficiency of this reaction.

FIG. 1.



The mercury vapour lamp with quartz condensing lenses was set up with a 5 cm. water-filter, and the light passed through a stop on to a cell with fused-on ends of plane-polished quartz containing the uranyl sulphate (0·01*M*) and oxalic acid (0·1*N*) solutions. The oxalic acid decomposed was estimated with *N*/20-potassium permanganate solution, and the total energy of the light measured with a Moll thermopile calibrated against a Hefner lamp (Gerlach, *Physikal. Z.*, 1913, **14**, 577). The amount of light absorbed was obtained from the difference in readings of the galvanometer connected to the thermopile when the quartz cell contained water or the solution. The results were as follows :

Galvanometer readings (1 division = $1{\cdot}4 \times 10^{-4}$ cal./sec.) :
Total energy of lamp falling on cell = 50 divisions.
Quartz cell filled with water = 30·5 „
„ „ „ „ solution = 17·5 „

Thus, cal. absorbed by solution per sec. = $2{\cdot}8 \times 10^{-3}$.
Taking the Hg line 3130 Å. as the mean wave-length absorbed, 1 gram-molecular quantum = 85,000 cal.; therefore the number of gram-molecular quanta absorbed per sec. = $3{\cdot}3 \times 10^{-8}$. In three experiments, each of 1 hour's exposure, the amount of oxalic

acid decomposed per second was 3·0, 3·35, and 3·5 × 10^{-8} g.-mol., respectively. From these results it appears that it may safely be assumed, in agreement with Büchi, that for each quantum of ultra-violet light absorbed one molecule of oxalic acid is decomposed.

The absorption of the aldehyde vapour was then measured by the difference in the photochemical change taking place in the uranyl sulphate–oxalic acid solution in the plane-walled quartz vessel E when the bulb A was empty and when it was filled with aldehyde vapour; also, by placing the vessel E in the place of A, the total amount of ultra-violet light could be measured.

Acetaldehyde undergoes two photochemical changes:

(1) Photolysis, $CH_3{\cdot}CHO = CH_4 + CO$.

(2) Polymerisation, $3CH_3{\cdot}CHO$ = paraldehyde + metaldehyde, etc.

The first series of measurements was made with a little liquid aldehyde in the bulb, *i.e.*, with saturated vapour, only the vapour being exposed to the light. If x molecules are changed according to reaction (1), the pressure change will be proportional to $2x$, the second reaction giving condensation products which do not affect the pressure appreciably. The results were:

Volume of reaction vessel = 125 c.c.

Pressure *increases* in cm. Hg after 1 hour's exposure. = {0·59, 0·665, 0·55, 0·685. Mean = 0·62.

Thus, $2x = 125 \times 0{\cdot}62/3600 \times 76 \times 23400 = 1{\cdot}2 \times 10^{-8}$ g.-mol./sec. or $x = 0{\cdot}6 \times 10^{-8}$ g.-mol./sec.

A second series of experiments was made with unsaturated vapour; a diminution in pressure then took place showing that more molecules are polymerised than photolysed. If y is the number of molecules activated for the reaction

$CH_3{\cdot}CHO$ (activated) + $2CH_3{\cdot}CHO$ = condensation products,

the diminution in pressure is proportional to $(3y - x)$. The results were:

Pressure *decreases* in cm. Hg. after 1 hour's exposure. = {3·5, 3·9, 3·3, 3·8, 2·8, 2·4. Mean 3·5.

Thus, $3y - x = 125 \times 3{\cdot}5/3600 \times 76 \times 23400 = 6{\cdot}85 \times 10^{-8}$ g.-mol./sec., whence $y = 2{\cdot}48 \times 10^{-8}$ g.-mol./sec.

Total number of g.-mols. activated per second for photolysis and polymerisation = $x + y = 3{\cdot}08 \times 10^{-8}$.

Number of gram-molecular quanta absorbed per second by aldehyde vapour (obtained from oxalic acid–uranyl sulphate solution titrations) = $1{\cdot}42 \times 10^{-8}$.

Allowing for the inaccuracy of the measurements and the complexity of the decomposition products of acetaldehyde, the results indicate that two molecules are chemically activated for each quantum absorbed.

Experiments with Acetone Vapour.

The same apparatus was used except that an air-bath was placed round the reaction bulb to keep the acetone as an unsaturated vapour at about 750 mm. and 60°. The amount of light absorbed was taken to be equal to that measured in the experiments on aqueous solutions of acetone described below, as, the concentrations of acetone being equal, it has been shown that the extinction coefficients of gaseous and of dissolved acetone are not very different (Porter and Iddings, *J. Amer. Chem. Soc.*, 1926, **48**, 40). The results were :

Vol. of bulb (c.c.).	Exposure (mins.).	Press. change (cm. Hg).	No. of g.-mols. acetone decomp. per sec.
125	245	2·42	$1·34 \times 10^{-8}$
80	160	3·63	$\}$ $1·81 \times 10^{-8}$
80	135	3·35	$\}$ (mean)

Number of gram-molecular quanta absorbed per sec. $= 1·0 \times 10^{-8}$.

Other experiments were made at room temperature in an apparatus consisting of two bulbs filled with acetone vapour connected by a U-tube containing liquid acetone. The apparatus was immersed in a thermostat before and after exposing one bulb (of quartz) to the lamp, and the photochemical change determined by the change in level of the liquid in the U-tube. The energy in the light absorbed was directly measured with the oxalic acid–uranyl sulphate solution. The results were :

Exposure = 1 hour. Volume of bulb = 125 c.c.

Pressure change (cm. Hg) = 0·212, 0·176, 0·141, 0·159, 0·247.

Taking the average as 0·187 cm. Hg, the number of g.-mol. of acetone decomposed per second is 2×10^{-9}. The mean of several oxalic acid titrations gave the number of gram-molecular quanta per second $= 4·85 \times 10^{-9}$. The number of molecules chemically changed is very close to the number of quanta absorbed.

The accuracy of these low-pressure measurements was not so great as that of the high-pressure ones, so that it is not certain whether the diminution in quantum sensitivity is real or due to experimental errors.

A further series of experiments was made with hot acetone vapour, oxalic acid–uranyl sulphate solutions being used to measure the absorption.

The results were : Volume of bulb = 125 c.c. Exposure = 60

minutes. Pressure change (cm. Hg.) = 0·60, 0·82, 0·815, 0·77, 0·71, 0·80, 0·60, 0·90.

Taking the mean as 0·75, the number of g.-mol. of acetone decomposed per second = $1·5 \times 10^{-8}$.

The mean of several oxalic acid titrations gave the number of gram-molecular quanta absorbed per second = $0·867 \times 10^{-8}$.

It seems that about two molecules of acetone are decomposed for each quantum absorbed.

Experiments with Aqueous Solutions of Acetone.

It is stated by Henri (*Compt. rend.*, 1913, **156**, 1012) that about 1300 molecules of acetone are hydrolysed for each quantum of ultra-violet light absorbed. He appears to have used an open quartz cell to contain the solution, and must have lost acetone by evaporation. In our experiments, solutions of acetone were exposed in a closed plane-walled quartz cell to an approximately parallel beam of ultra-violet light, and the number of quanta absorbed measured with the oxalic acid–uranyl sulphate solution. When the acetone solution was titrated iodimetrically, the photochemical change was too small to be measurable, although if the reaction followed the Einstein–Stark law it should have been recognisable. The acetic acid formed was therefore estimated with very dilute baryta solution, and the following mean results were obtained :

Conc. of acetone solution %.	G.-mols. acetic acid formed per sec.	G.-molecular quanta absorbed per sec.
0·3	$5·7 \times 10^{-10}$	$1·0 \times 10^{-8}$
15	$2·88 \times 10^{-9}$	$1·9 \times 10^{-8}$

Here the number of g.-mols. of acetic acid formed is less than one-fifth of the number of quanta absorbed. It is possible that formation of other products occurs, but these could not be discovered or estimated, and the results must be taken to be in serious disagreement with those of Henri.

These measurements emphasise the need for reinvestigation of older results on the ratio of the number of molecules reacting to the number of quanta absorbed in photochemical reactions. Correcting the tables of such reactions examined from this point of view which were presented to the Faraday Society in October, 1925 (Allmand, Dhar, and Mukerji), we now find that in 65% of the cases the number of molecules reacting is, within a factor of about 3, equal to the number of molecules physically activated, indicating fairly simple mechanisms in all these examples. In 20% of the cases, chiefly those involving halogen molecules, the number of molecules changed is many times the number of quanta absorbed, indicating " chain " mechanisms. It is characteristic

of this class of reaction that "inhibitors" produce their large effect by interfering with the "chains." In 15% of the cases, the number of molecules reacting is much less than the number of quanta absorbed, and in some of these cases, again involving the halogens, we find long lives of activated molecules (Briers, Chapman, and Walters, this vol., p. 562; Eggert, *Physikal. Z.*, 1925, **26**, 865), and reaction rates varying with the square root of the light absorbed (Bodenstein and Lütkemeyer, *Z. physikal. Chem.*, 1924, **114**, 208; Berthoud and Bellenot, *J. Chim. phys.*, 1924, **21**, 308), all indicating a primary dissociation of the halogen molecule, followed by extensive slow recombination of the atoms produced, only an occasional atom entering into the observed chemical change. There is need for much work to elucidate the complexities of these last two classes of reactions. It is significant, however, that the first class of reactions should be the largest; here apparently every molecule physically activated takes part in chemical change, showing that under these conditions, when a molecule is activated, its chemical reactivity on collision is not affected by its orientation.

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CCXI.—*The Constitution of the Condensation Product of β-Phenylhydroxylamine and Acetone.*

By FRANCIS HARROLD BANFIELD and JOSEPH KENYON.

A CONCENTRATED solution of β-phenylhydroxylamine in acetone deposits, after about two weeks, large, rhombic crystals which melt at 136°. To this compound Bamberger and Rudolf, who first described it (*Ber.*, 1907, **40**, 2237), gave the constitution $Me_2C\!\!<\!\!\begin{matrix}NPh\\O\end{matrix}$ by analogy with $PhCH\!\!<\!\!\begin{matrix}NPh\\O\end{matrix}$,* at that time regarded as the constitution of the condensation product of β-phenylhydroxylamine and benzaldehyde. Beckmann and Scheiber (*Annalen*, 1907, **355**, 235) showed, by molecular-weight determinations, that the empirical formula must be doubled, and prepared analogous

* Bamberger subsequently (*Ber.*, 1922, **55**, 3376; 1924, **57**, 2082) replaced this formula by PhCH:NPh:O in accordance with the modern formulation of azoxy-compounds, and support for the new constitution is afforded by the formation of the additive compound $\begin{matrix}CHPh\cdot NPh\\|\quad\quad\rangle O\\NPh—CO\end{matrix}$ with phenylcarbimide.

compounds from acetone and β- *p*- and *m*- (but not *o*-) tolyl- and β-(α-naphthyl)-hydroxylamines. They did not succeed, however, in preparing condensation compounds when acetone was replaced by its homologues. Scheiber and Wolf (*Annalen*, 1908, **357**, 25), who studied the reaction products of acetone and these β-arylhydroxylamines in some detail, suggested that the condensation is due to loss of water following direct combination of the two reagents; *e.g.*,

$$2CMe_2{<}^{OH}_{NPh\cdot OH} \longrightarrow O{<}^{NPh\cdot CMe_2}_{NPh\cdot CMe_2}{>}O \text{ or } O{<}^{NPh\cdot CMe_2}_{CMe_2\cdot NPh}{>}O.$$

They did not, however, prepare any crystalline derivatives or well-defined decomposition products in support of either of these formulæ.

Although, as stated by Scheiber and Wolf (*loc. cit.*), the condensation product of β-phenylhydroxylamine and acetone is very susceptible to acidic reagents, yet it is possible by working under carefully regulated conditions to prepare a number of its crystalline derivatives and other definitely characterised products. The formation of these is in no way accounted for by the formulæ given above.

The maximum yield of the condensation product—68%—is obtained by the interaction, at the ordinary temperature, of dry β-phenylhydroxylamine and acetone during a period of two to three months. Reaction at a higher temperature results in rapid decomposition of the β-phenylhydroxylamine, and the effect of adding calcium chloride or sodium sulphate to the reaction mixture to combine with the liberated water is to diminish the yield of the condensation product.

The filtrate after removal of the condensation product consists of two layers: (*a*) water, (*b*) an acetone solution of azoxybenzene and aniline. The latter two substances are the normal decomposition products of β-phenylhydroxylamine and can be isolated in amounts almost sufficient to account for the portion of the β-phenylhydroxylamine which does not condense with acetone. The probable course of the reaction between acetone and β-phenylhydroxylamine may therefore be represented by the equation $2Me_2CO + 2PhNH\cdot OH = C_{18}H_{22}O_2N_2 + 2H_2O$.

The condensation product decomposes slowly in solution at the ordinary temperature; when a solution in 96% alcohol is boiled for 24 hours, complete decomposition into mesityl oxide, aniline, and azoxybenzene occurs.

The condensation product reacts readily at the ordinary temperature with acetic anhydride to yield a crystalline *monoacetyl*

derivative, $C_{20}H_{24}O_3N_2$, and in pyridine solution with benzoyl chloride to give a crystalline *monobenzoyl* derivative, $C_{25}H_{26}O_3N_2$. These results alone suffice to show the incorrectness of the formulæ mentioned above, since none of them contains a reactive hydrogen atom which would be likely to undergo displacement by an acyl group. The acyl derivatives are readily and quantitatively converted into the original condensation product on hydrolysis and therefore are very probably derivatives of it and not of some transformation compound.

The introduction of an acyl group into the molecule of the condensation product renders it resistant to permanganate and other oxidising agents and to dilute acids—including acetic acid—which attack it readily. The acyl group evidently protects a very reactive portion of the molecule, and since it can be removed by warming for a few minutes with alcoholic potash, there is a strong presumption that the group so protected is a hydroxyl group. Additional evidence for the presence of a hydroxyl group is afforded by the production at the ordinary temperature of a *potassium* derivative, $C_{18}H_{21}O_2N_2K$, which reacts with benzoic anhydride to give the benzoyl derivative described above. That the hydroxyl group is attached to nitrogen is rendered probable by the ease with which this potassium derivative is quantitatively oxidised by air to a red *compound*, $C_{18}H_{21}O_2N_2$ (see p. 1622).

Action of Dilute Hydrochloric Acid on the Condensation Product.—The finely-powdered material is readily decomposed by dilute hydrochloric acid, the principal product being a liquid *base*, $C_{12}H_{16}ONCl$; small quantities of azobenzene, β-phenylhydroxylamine and *p*-chloroaniline and a trace of mesityl oxide are also produced. This base differs in composition from the original compound by C_6H_6ONCl, and this fact and the nature of the by-products indicate that one of the β-phenylhydroxylamine residues has been detached from the compound during the reaction. Moreover, the acquisition of a chlorine atom under such mild treatment is in harmony with the view that a hydroxyl group attached to a nitrogen atom has been replaced by a chlorine atom: $\cdot NPh\cdot OH + HCl \longrightarrow \cdot NPhCl$. The chloro-base thus produced does not, however, liberate iodine from an acidified solution of potassium iodide, so it is necessary to assume that the chlorine atom has already migrated into the benzene nucleus. This view is confirmed by the behaviour of the chloro-base, which decomposes into *p*-chloroaniline and mesityl oxide in molecular proportions on heating and gives equivalent quantities of *p*-chloroacetanilide and mesityl oxide by interaction with acetic anhydride. Moreover, it reacts with nitrous acid to give a yellow crystalline *nitrosoamine* (m. p. 75—76°)—a result

which further supports the view that the chlorine atom has wandered * from the nitrogen atom to the nucleus.

The production of mesityl oxide and *p*-chloroaniline in equivalent proportions accounts entirely for the molecule of the chloro-base—$C_{12}H_{16}ONCl = C_6H_{10}O + C_6H_6NCl$—and several attempts have been made, though unsuccessfully, to synthesise it from these two compounds.

The chloro-base readily yields a crystalline *semicarbazone* ($C_{13}H_{19}ON_4Cl$), the oxygen atom thus being shown to be ketonic, and by its reduction with sodium and alcohol sodium chloride and aniline are obtained in equivalent quantities together with *p*-chloroaniline and methyl*iso*butylcarbinol. There can be little doubt, therefore, that the constitution of the chloro-base is represented by formula (I), and its modes of decomposition by heat and by acetic anhydride by the scheme :

$$\underset{\text{(I.)}}{C_6H_4Cl\cdot NH\cdot CMe_2\cdot CH_2\cdot COMe} \xrightarrow{\text{heat}} CMe_2{:}CH\cdot COMe + C_6H_4Cl\cdot NH_2.$$

$$\xrightarrow{Ac_2O} CMe_2{:}CH\cdot COMe + C_6H_4Cl\cdot NHAc + AcOH.$$

Its formation from the original compound can be represented by the equation :

$$C_{18}H_{22}O_2N_2 + HCl = C_6H_4Cl\cdot NH\cdot CMe_2\cdot CH_2\cdot COMe + NHPh\cdot OH.$$

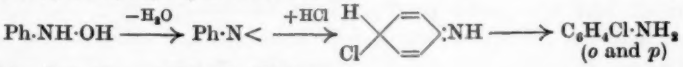
The constitution of the chloro-base as β-p-*chloroanilino*-β-*methylpentan*-δ-*one* has been established by its synthesis from β-phenylhydroxylamine and mesityl oxide by the following reactions :

$$\begin{matrix} CMe_2{:}CH\cdot COMe \\ NHPh\cdot OH \end{matrix} \longrightarrow \underset{\text{(II.)}}{\begin{matrix} CMe_2\cdot CH_2\cdot COMe \\ NPh\cdot OH \end{matrix}} \xrightarrow{HCl} \begin{matrix} CMe_2\cdot CH_2\cdot COMe \\ NH\cdot C_6H_4Cl \end{matrix}$$

The compound (II) is too unstable to be isolated; its *sodium* derivative, however, has been prepared by the interaction of mesityl oxide and the sodium derivative of β-phenylhydroxylamine.

The complete and facile scission, by the action of dilute hydrochloric acid, of a molecule of β-phenylhydroxylamine from the original condensation product renders it probable that the latter is β-*phenyl*-

* The mechanism of the formation of *p*-chloroaniline from β-phenylhydroxylamine and hydrochloric acid is represented by Bamberger (*Ber.*, 1900, **33**, 3600; 1901, **34**, 61) as follows :.

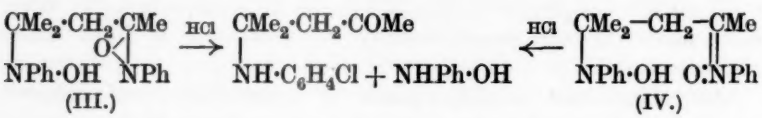


and by Löb (*Ber.*, 1896, **29**, 1894) as

$$Ph\cdot NH\cdot OH + HCl \longrightarrow Ph\cdot NHCl \longrightarrow C_6H_4Cl\cdot NH_2.$$

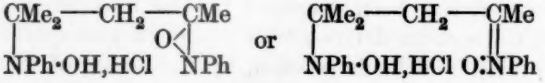
The experimental results recorded above are clearly opposed to Bamberger's view and in agreement with Löb's.

hydroxylamino-β-methylpentan-δ-oneoxime N-*phenyl ether* (III), or β-*phenylhydroxylamino-β-methylpentane-δ-phenylimine oxide* (IV), and its interaction with hydrochloric acid may be represented thus:



This view of the constitution of the condensation product is supported by the following additional reactions. The condensation product is rapidly decomposed by hot concentrated hydrochloric acid, giving mesityl oxide (20·5%), *p*-chloroaniline (33%) and azoxybenzene (16%) together with a small amount of a substance of very high boiling point. A similar decomposition is effected by steam, the principal products being azoxybenzene, mesityl oxide, and tarry material which has not been identified. When heated with an alcoholic solution of zinc chloride, the condensation product decomposes into *p*-phenetidine, azoxybenzene, *p*-chloroaniline, aniline and mesityl oxide. A similar scission of the molecule is brought about by the prolonged action of cold dilute sulphuric acid, the products being *p*-aminophenol, mesityl oxide and azoxybenzene; these can be isolated in amounts which account for 80% of the original material.

In marked contrast to the above-mentioned hydrolytic agents, hydrogen chloride converts the condensation product in dry ethereal solution into its *monohydrochloride*, a white solid which is decomposed by water into its components. This compound resembles β-phenylhydroxylamine hydrochloride in its behaviour and its constitution is probably



Reduction of the Condensation Product.—The condensation product is unaffected in moist ethereal solution by aluminium amalgam. It is, however, readily reduced in absolute alcoholic solution by sodium; aniline, azobenzene, and methyl*iso*butylcarbinol are formed, but the main product is a secondary *base*, $C_{12}H_{19}ON$, from which a *chloroplatinate*, a yellow, crystalline *nitrosoamine*, and a *diacetyl* derivative have been prepared. Since one of the acetyl groups in this derivative is much more easily removed by hydrolysis than the other, it is probable that the secondary base contains a

hydroxyl group. Two formulæ for this compound suggest themselves:

$$NHPh\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OH \quad \text{and} \quad CHMe_2\cdot CH_2\cdot CMe(OH)\cdot NHPh,$$

of which the former is the more probable, as it implies a decomposition of the condensation product similar to that brought about by hydrolytic agents. The alternative formula is improbable, since a compound of this structure would tend to be dehydrated by an excess of an acetylating agent.

Several unsuccessful attempts were made to synthesise the secondary base from aniline and mesityl oxide. The only definite compound which could be isolated appeared to be produced by the condensation of one molecule of mesityl oxide with two molecules of aniline.

Action of Oxidising Agents on the Condensation Product.—When the finely powdered condensation product is agitated with a solution of potassium permanganate, potassium ferricyanide, sodium hypobromite, or ammoniacal silver oxide, or is exposed, suspended in faintly alkaline water, to the air for several weeks, it is oxidised to a bright red, crystalline compound. The most convenient procedure, however, is by the use of ammoniacal silver oxide as described in the experimental section. The oxidised compound, which is easily obtained pure in a yield of 98% of the theoretical amount, is produced by the action of one-half molecular quantity of silver oxide, it thus being shown that only one atom of hydrogen is removed from each molecule of the condensation product. Its molecular weight is of the same order of magnitude (about 300) as that of the unoxidised compound and therefore there has been no condensation between two molecules of the latter with the elimination of hydrogen. Moreover, the two compounds are almost identical in composition and therefore no oxygen has entered the original substance. That no change other than oxidation occurs during the reaction is shown by the quantitative regeneration of the original compound by the action of aluminium amalgam on a cold moist ethereal solution of the red oxidation compound.

The oxidised and the unoxidised compound differ in several important properties. The former does not react with acetic anhydride or with benzoyl chloride in pyridine solution at the ordinary temperature, the absence of a hydroxyl group being thus indicated. This view is supported by the marked difference in the behaviour of cold dilute hydrochloric acid towards the two compounds; whereas the oxidised compound is unaffected by this reagent (and other cold dilute mineral acids), the unoxidised one

undergoes an immediate change involving the substitution of one atom of chlorine for one atom of hydrogen and one of oxygen—a type of reaction to which β-arylhydroxylamines are peculiarly susceptible. It is therefore probable that the oxidation process involves the reaction

$$2\,{}^{Ph}_{Ph}\!>\!C\!<\!N\cdot OH + O = 2\,{}^{Ph}_{Ph}\!>\!C\!<\!N{:}O + H_2O$$

and leads to the production of a compound which contains a quadrivalent nitrogen atom.

Additional support for this view is furnished by the following experimental evidence: (*a*) one of the hydrolytic products of the action of dilute hydrochloric acid on the original condensation compound is β-phenylhydroxylamine (see p. 1623), whilst the oxidised compound in dry ethereal solution combines with hydrogen chloride to give a derivative the decomposition of which by water yields 50% of the unoxidised compound and 10% of nitrosobenzene (*i.e.*, oxidised β-phenylhydroxylamine); (*b*) the oxidised compound is immediately decomposed by steam, giving a mixture of products from which the original unoxidised compound (22%) and nitrosobenzene (13%) can be isolated; (*c*) when the oxidised compound is gently heated under diminished pressure, it decomposes and nitrosobenzene sublimes from the reaction products.

Since both the unoxidised and the oxidised compound yield under the action of hot dilute mineral acids, or even of hot water, considerable quantities of mesityl oxide, the structural similarity of the aliphatic portions of the two molecules is confirmed. The oxidation process may therefore be expressed by the equation

$$2\,\begin{array}{l}CMe_2\text{—}CH_2\text{—}CMe\\ \quad\vert\qquad\quad O\!<\!\vert\\ NPh\cdot OH\qquad NPh\end{array} + Ag_2O = \begin{array}{l}CMe_2\text{—}CH_2\text{—}CMe\\ \quad\vert\qquad\quad O\!<\!\vert\\ NPh{:}O\qquad NPh\end{array} + 2Ag + H_2O$$

β(phenylnitrogen oxide)-*β*-methylpentane-δ-oneoxime *N*-phenyl ether.

and the decomposition of the two compounds by the equations

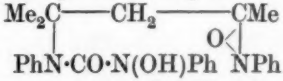
$$4\,\begin{array}{l}CMe_2\cdot CH_2\cdot CMe\\ \quad\vert\qquad\quad O\!<\!\vert\\ NPh{:}O\qquad NPh\end{array} + 2H_2O = 2\,\begin{array}{l}CMe_2\cdot CH_2\cdot CMe\\ \quad\vert\qquad\quad O\!<\!\vert\\ NPh\cdot OH\quad NPh\end{array} + 3NHPh\cdot OH + PhNO + 2CMe_2{:}CH\cdot COMe$$

$$2\,\begin{array}{l}CMe_2\cdot CH_2\cdot CMe\\ \quad\vert\qquad\quad O\!<\!\vert\\ NPh\cdot OH\quad NPh\end{array} + 2H_2O = 2CMe_2{:}CH\cdot COMe + 4NHPh\cdot OH.$$

The experimental results so far recorded do not enable a decision to be made between the oxime-ether and the nitrone formulations of the condensation compound. The following results are in harmony with the first view, but since the evidence is of a negative

character the question is not considered settled. Attempts are being made to obtain further evidence on this point.

The condensation product forms an additive compound with phenylcarbimide (1 mol.)—a result which is not obtained with either its acetyl derivative or its oxidation product. All the experimental evidence points to these two derivatives having the same molecular structure as the parent compound with the sole modification that a >N·OH group has been converted in the one case into $>N\cdot O\cdot CO\cdot CH_3$ and in the other into >N:O. It is highly probable, therefore, that phenylcarbimide reacts with the >N·OH part of the condensation product to give a compound



which is analogous to β-carbanilino-β-phenylhydroxylamine, NHPh·CO·N(OH)Ph, produced by the interaction of phenylcarbimide and β-phenylhydroxylamine (Beckmann, *J. pr. Chem.*, 1897, **56**, 71).

It follows also that there is present in the condensation product no other group capable of reacting with phenylcarbimide.

Evidence for the view that the condensation products of β-phenylhydroxylamine with acetone and with benzaldehyde differ in structure is the fact that the latter product is unaffected by cold concentrated hydrochloric acid or 65% sulphuric acid, reagents which hydrolyse the acetone compound with the greatest readiness.

One of the very few recorded cases of organic compounds which contain quadrivalent nitrogen is diphenylnitric oxide, which Wieland and Offenbächer (*Ber.*, 1914, **47**, 2111) obtained by the oxidation of ββ-diphenylhydroxylamine with silver oxide:

$$2Ph_2N\cdot OH + O = 2Ph_2N{:}O + H_2O \quad . \quad . \quad . \quad (1)$$

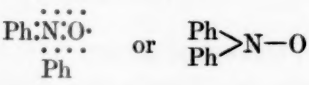
Diphenylnitric oxide is described as an intensely red substance which decomposes on keeping; liberates iodine from an acidified solution of potassium iodide; is reduced by phenylhydrazine to the original ββ-diphenylhydroxylamine and by stronger reducing agents to diphenylamine; and is converted by the action of dilute hydrochloric acid, by simultaneous oxidation and reduction, into diphenylamine and quinoneanil oxide—a change which sometimes occurs spontaneously in ethereal solution (Wieland and Roth, *Ber.*, 1920, **53**, 215):

$$2Ph_2N{:}O = Ph_2NH + PhN{:}C_6H_4{:}O.$$

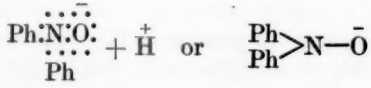
There are, therefore, many points of similarity between diphenylnitric oxide and the red compound formed by the oxidation of the

condensation product of β-phenylhydroxylamine and acetone, in which the presence of a quadrivalent nitrogen atom has been suggested.

The formulation of the oxidation of diphenylhydroxylamine to diphenylnitric oxide as in equation (1) is in conflict with the electronic theory. The reaction is, however, of some interest, since the oxygen atom which takes part in the reaction gains two electrons and acquires them from two molecules of the hydroxylamine. Obviously, therefore, each molecule of diphenylhydroxylamine loses one electron, and the product of oxidation has, according to the electronic theory, the formula



and can be contrasted with diphenylhydroxylamine which has "ionised":



The particular type of N—O compound formed by the oxidation of the condensation product of acetone and phenylhydroxylamine belongs, therefore, to the small class of substances whose molecules contain an uneven number of electrons—the so-called "odd electron molecules"—of which nitrogen dioxide is the most typical example; others are nitric oxide, triphenylmethyl, and chlorine dioxide. Lewis states that "odd electronic compounds" with the exception of nitric oxide absorb light in the visible part of the spectrum and are generally intensely coloured. They are very reactive and attach themselves to a great variety of substances; they tend to react in such a manner that one molecule gains an electron while another loses one (simultaneous oxidation and reduction). The red oxidation product thus appears to possess the properties of an odd electron compound, and, indeed, its method of preparation combined with the determination of its molecular weight proves that it is such a substance.

Experimental.

Preparation of the Condensation Product.—β-Phenylhydroxylamine, prepared by Kamm's method ("Organic Syntheses," IV, 57) in 60% yield, was dissolved in rather more than its own weight of dry acetone, and the filtered solution was kept for several days at room temperature; the condensation product then began to

crystallise. Thereafter the mixture was kept, with daily agitation, in the ice-chest for 3 months, until no further separation occurred. The yield of the condensation product varied from 40—68% (calculated on the amount of β-phenylhydroxylamine), the better yields being obtained when carefully dried β-phenylhydroxylamine was used. The condensation product, after being washed with cold acetone, in which it was only slightly soluble, was obtained almost colourless. It crystallised from ethyl alcohol in hard, glassy rhombs, m. p. 136° (slight decomp.). In a typical experiment, 5704 g. of β-phenylhydroxylamine dissolved in acetone (6830 c.c.) gave, after several weeks, 3719 g. of the condensation product (yield 49%).

The reaction mixture, when left undisturbed and "unseeded," deposits the condensation product in large, colourless, transparent, glassy rhombs which remain colourless and retain the same melting point (136°) for several years. The small crystals obtained by frequent agitation of the solution slowly develop, during several months, a pale yellow colour and a slight odour: this is probably due to their retaining a small quantity of the mother-liquor.

Earlier workers state that this compound melts with decomposition. The amount of decomposition, however, is very small, for a molten sample will resolidify and then melt at a temperature only a few degrees below the original melting point; after one crystallisation from alcohol, it melts at 136°.

The Acetyl Derivative.—(a) To the deep brownish-orange solution obtained by shaking the finely powdered condensation product (10 g.) with pure acetic anhydride (10 c.c.) below 35°, ice is gradually added; the whole then sets to a crystalline mass. The washed and dried product (12 g.) melts at 95—97°.

(b) To a solution of the condensation product (45 g.) in pyridine (60 c.c.) acetic anhydride is added (23 c.c.) at such a rate that the temperature does not rise above 45°. After a few minutes, crushed ice is added, and the crude acetyl derivative washed and dried as before (yield, about 54 g.).

The *acetyl* derivative separates from ethyl acetate, acetone, or aqueous alcohol in radiating clusters of prismatic needles, m. p. 99—101°. When it is added to warm benzene a cloudy solution is produced which becomes clear on the addition of calcium chloride. This solution, when diluted with warm light petroleum, deposits stout needles. These melt at 105—106° (without decomp.), but at about 140° vigorous decomposition sets in and tarry products are formed (Found in material crystallised from alcohol: C, 66·95; H, 7·2; N, 7·7; CH_3·CO, 12·6. $C_{20}H_{24}O_3N_2,H_2O$ requires C, 67·0; H, 7·3; N, 7·8; CH_3·CO, 12·0%. Found in material crystallised

from benzene: C, 71·0; H, 7·1; *M*, cryoscopic in benzene, 310. $C_{20}H_{24}O_3N_2$ requires C, 70·6; H, 7·1%; *M*, 340).

The acetyl derivative was recovered unchanged after 1 g. had been heated with acetic anhydride (3 c.c.) at 100° for 10 minutes.

The Benzoyl Derivative.—(a) A solution of the condensation product (12 g.) and benzoyl chloride (6 g.) in pyridine (50 c.c.) is, after several hours, mixed with crushed ice. The washed and dried crystalline product, m. p. 90—95°, is obtained in almost quantitative yield.

(b) A suspension of the potassium derivative of the condensation product (see below) in pure dry ether is shaken with benzoic anhydride (1 mol.) for 15 minutes, the gelatinous precipitate of potassium benzoate filtered off and washed with dry ether, and the filtrate concentrated; the benzoyl derivative is thus obtained as an orange oil which solidifies completely on inoculation.

The *benzoyl* derivative crystallises from aqueous alcohol in rosettes of glistening, prismatic needles, m. p. 96—98°, containing $1H_2O$ (Found: C, 71·0; H, 6·9; N, 6·6. $C_{25}H_{26}O_3N_2,H_2O$ requires C, 71·4; H, 6·7; N, 6·7%) and from benzene or light petroleum in anhydrous, prismatic needles, m. p. 98—99° (Found: C, 74·6; H, 6·4. $C_{25}H_{26}O_3N_2$ requires C, 74·6; H, 6·4%).

Hydrolysis. To a solution of the benzoyl derivative (1·1 g.) in warm alcohol (10 c.c.), sodium hydroxide (0·2 g.) was added, followed, after 10 minutes, by water. The crystalline product, m. p. 135—136°, weighed 0·62 g. (calc., 0·78 g.) and from the concentrated acidified filtrate 0·25 g. of benzoic acid was obtained (calc., 0·32 g.).

The *potassium* derivative is prepared by adding a benzene solution of the condensation product to rather less than one atomic proportion of finely powdered potassium. The latter dissolves, hydrogen is evolved, the liquid darkens, and a white gelatinous precipitate forms. This is filtered off, washed quickly with dry benzene several times, and dried in a vacuum (Found: K, 11·7, 11·8. $C_{18}H_{21}O_2N_2K$ requires K, 11·3%). When left for several days in a dry atmosphere, the substance (1·1 g.) develops an orange colour and, on treatment with water, gives an orange powder, m. p. about 90°. After crystallisation from alcohol, this powder is obtained in fine red needles (1·0 g.); these, alone or mixed with an authentic specimen of the red oxidation product, melt at 89—90°.

By passing hydrogen chloride into a dry ethereal solution of the condensation product, its *monohydrochloride* is obtained as a white solid which, after being washed with ether and dried in a vacuum, melts at 62—64° and at 80° undergoes vigorous decomposition

(Found : HCl, 11·1. $C_{18}H_{22}O_2N_2$,HCl requires HCl, 10·9%). The solid is stable in a vacuum for some hours, but on exposure to air turns black. It is decomposed by water with regeneration of the original condensation product in an almost pure condition.

Formation of β-p-*Chloroanilino*-β-*methylpentan*-δ-*one from the Condensation Product.*—The freshly recrystallised and finely powdered condensation product (50 g.) is shaken for 2 hours with *N*-hydrochloric acid (400 c.c.). The pale yellow solution is filtered from undissolved material (4—8 g.) and extracted three times with ether to remove azoxybenzene, mesityl oxide and a small quantity of β-phenylhydroxylamine. The acid solution is rendered alkaline and the precipitated bases (35—40 g.), after extraction and drying, are distilled under 15 mm. pressure. Two main fractions are obtained, (i) up to 150°, (ii) 150—180°. The first contains water (if the receiver has been cooled in ice), mesityl oxide, *p*-chloroaniline, and a proportion of the higher-boiling base. The second fraction, which weighs about three times as much as the first and contains the *chloro-base*, is dissolved in ether and the solution is washed with successive small quantities of dilute hydrochloric acid; thereafter a mixture (4·8 g.) of azobenzene and azoxybenzene (1 : 4) is obtained from it. The hydrochloric acid solution is rendered alkaline, the precipitated chloro-base (20 g.) is extracted with ether and twice redistilled, and a fraction collected at 169—172°/11 mm. or at 133—136° under the pressure attained with a mercury vapour pump. It is a golden-yellow liquid which shows no tendency to solidify (Found : C, 63·5; H, 7·3; N, 6·3; Cl, 15·7. $C_{12}H_{16}ONCl$ requires C, 63·8; H, 7·1; N, 6·2; Cl, 15·7%). The *nitrosoamine*, obtained by means of sodium nitrite and ice-cold, dilute hydrochloric acid, crystallises from ether–petrol in rosettes of pale yellow needles, m. p. 75—76° after softening at 70° (Found : N, 11·2. $C_{12}H_{15}O_2N_2Cl$ requires N, 11·0%).

The chloro-base readily yields a *semicarbazone*, which crystallises from alcohol in microscopic, flat prisms, m. p. 125° (Found : N, 20·2. $C_{13}H_{19}ON_4Cl$ requires N, 19·8%).

Action of Sodium and Alcohol on the Chloro-base.—To a solution of the base (5 g.) in warm alcohol, sodium (3 g.) is added in small pieces; a precipitate of sodium chloride forms. By working up the product in the usual way, there is obtained a non-basic fraction (1·7 g.), b. p. 128—133°, with a camphoraceous odour; this, after treatment with semicarbazide to remove a little unreduced mesityl oxide as its semicarbazide semicarbazone (m. p. 220°), distils at 130—134° and reacts with *p*-nitrobenzoyl chloride in pyridine solution to give a crystalline *p*-nitrobenzoic ester which melts at 24—26° either alone or when mixed with methyl*iso*butylcarbinyl

p-nitrobenzoate. The basic portion of the product consists of unchanged chloro-base (0·5 g.), *p*-chloroaniline (1·0 g.), and aniline (0·9 g.). The chlorine present as sodium chloride in the aqueous portion, estimated volumetrically, is 0·36 g., corresponding to 0·93 g. of aniline. The substance therefore contains one aniline residue for each atom of chlorine present in the molecule.

Decomposition of β-p-*Chloroanilino*-β-*methylpentan*-δ-*one by Acetic Anhydride.*—The chloro-base (1·5 g.) is warmed for 15 minutes with an equal weight of acetic anhydride, and the cooled reaction mixture diluted with water (60 c.c.). The crystalline solid, after being washed and dried (0·96 g.), melts at 172—174°, alone or mixed with *p*-chloroacetanilide (Found: N, 8·2. Calc.: N, 8·1%). The filtrate contains a few globules of mesityl oxide (b. p. 126—130°).

Synthesis of β-p-*Chloroanilino*-β-*methylpentan*-δ-*one.*—(a) A solution of β-phenylhydroxylamine (168 g.) and mesityl oxide (148 g.) in just sufficient dry ether is kept for a month and then shaken for 3 hours with *N*-hydrochloric acid (400 c.c.). The acid layer is separated, extracted three times with ether, and rendered alkaline with sodium hydroxide, and the precipitated base is extracted, dried, and distilled; the principal fraction, b. p. 160—175°/15 mm., gives, after four distillations, a fraction (40 g.), b. p. 172—175°/13 mm. (Found: N, 6·3; Cl, 15·7. Calc. for $C_{12}H_{16}ONCl$: N, 6·2; Cl, 15·7%). During distillation the base undergoes slight decomposition into mesityl oxide and *p*-chloroaniline.

The semicarbazone, prepared in the usual manner, crystallises from alcohol in microscopic, flat prisms, m. p. 124—125°.

(b) The gelatinous sodium derivative of β-phenylhydroxylamine obtained from sodium (1 equiv.) and phenylhydroxylamine (20 g.) in dry ethereal solution dissolves on addition of mesityl oxide (1 mol.), heat is developed, and a precipitate slowly separates. After 10 days, this is filtered off, quickly washed with dry ether, and dried (wt. 10 g.) (Found: Na, 11·5. $C_{12}H_{16}O_2NNa$ requires Na, 10·0%). The compound evidently contains unchanged sodium derivative of β-phenylhydroxylamine (Na, 17·6%). It is very hygroscopic and decomposes on standing. It is decomposed by water, and the liberated compound is converted by cold dilute hydrochloric acid into β-*p*-chloroanilino-β-methylpentan-δ-one. This synthetic chloro-base yields a semicarbazone which melts at 125° either alone or when mixed with the semicarbazone of the chloro-base obtained by the action of dilute hydrochloric acid on the original condensation compound. Acetic anhydride decomposes it into mesityl oxide and *p*-chloroacetanilide.

Behaviour of the Condensation Product.—(a) *Towards hot hydro-*

chloric acid. A current of steam is passed into a mixture of the condensation product (100 g.) and concentrated hydrochloric acid (100 c.c.); rapid decomposition takes place and mesityl oxide (20·5 g.) distils with the steam. From the non-volatile product, *p*-chloroaniline (33 g.), azoxybenzene (16 g.), and a non-basic material of high boiling point (2 g.) are obtained.

(b) *Towards steam.* A rapid current of steam is passed over the finely powdered compound (20 g.). An oil distils with the first 6 l. of water, leaving a black tar (5 g.). The oil sets, on cooling, to a crystalline mass of azoxybenzene (9·7 g.). Extraction of the aqueous distillate yields mesityl oxide (2·5 g.).

(c) *Towards an alcoholic solution of zinc chloride.* Zinc chloride (50 g.), the condensation product (50 g.), and ethyl alcohol (250 c.c.) are heated together under reflux for 30 minutes. After cooling, the crystalline material is filtered off and recrystallised from alcohol, glistening leaflets (9·2 g.), m. p. 237—239°, of p-*phenetidine zincichloride* being obtained [Found: Zn, 15·6; Cl, 17·4; C, 46·3; H, 5·7. $(EtO\cdot C_6H_4\cdot NH_2)_2,ZnCl_2$ requires Zn, 15·8; Cl, 17·2; C, 46·6; H, 5·3%]. From the mother-liquor, aniline (2 g.), *p*-chloroaniline (10 g.), azoxybenzene * (11·5 g.), and mesityl oxide (3 g.) are isolated. Much of the last substance is undoubtedly lost owing to its low boiling point (40°) at the pressure employed.

The zincichloride yields phenacetin when it is heated with acetic anhydride, and *p*-phenetidine hydrochloride, m. p. 236—237°, when heated with hydrochloric acid.

Preparation of the Red Oxidation Compound.—A mixture of the finely powdered condensation product (59·6 g.), light petroleum, b. p. 40—60° (1500 c.c.), and an ammoniacal solution of silver oxide (from 36 g. of silver nitrate) is mechanically shaken for 48 hours; oxidation commences almost at once, the petroleum solution turning bright red and metallic silver being deposited. The petroleum layer is separated from the filtered liquid, washed with water, dried, and evaporated slowly in a bath of warm water (to avoid overheating), until crystallisation sets in. The solid on the filter is washed with water until free from ammonia, air-dried, and repeatedly extracted with dry ether; the extracts are evaporated to small bulk and diluted with light petroleum until crystallisation sets in. About one-third of the oxidation product is contained in the original petroleum solution, the remainder having crystallised

* It is stated in the literature (Meyer and Jacobson, "Organische Chemie," II, 251; Beilstein, "Organische Chemie," IV, 1335) that azoxybenzene decomposes on heating. We have found that it distils quite readily at 191°/12 mm. with only slight decomposition. The pale yellow distillate sets completely to a mass of long, hair-like needles, m. p. 35°.

and become mixed with the metallic silver. The yield is 58·4 g. (98% of the theoretical).

This substance crystallises from petroleum in compact, hemispherical clusters of bright red, glistening prisms which melt and decompose at 88—90°, producing a black liquid which does not resolidify [Found : C, 72·7; H, 7·15; N, 9·4; *M*, cryoscopic in benzene, 276 (mean of four values). $C_{18}H_{21}O_2N_2$ requires C, 72·7; H, 7·1; N, 9·4%; *M*, 297].

Determinations of the molecular weight of the oxidised compound in acetone by the ebullioscopic method gave values ranging from 285 to 325, but little reliance can be placed upon these, as some decomposition occurred in the hot solution. After evaporation of the acetone, the residue had a strong odour of nitrosobenzene and contained crystals of the original unoxidised condensation product of m. p. 135—136°.

Reactions of the Red Oxidation Compound.—(a) *Reduction.* The compound in ethereal solution is quantitatively reduced to the original condensation product by (*a*) zinc dust and dilute caustic soda solution, (*b*) aluminium amalgam, (*c*) phenylhydrazine. The product melts at 133—136° and 136° before and after crystallisation, respectively.

By the action of potassium iodide and dilute acetic acid on an ethereal solution of the oxidation compound the original condensation product is obtained in 77% yield, the remaining material being a dark, thick oil from which nothing crystalline can be isolated.

(b) *Action of heat.* A rapid current of steam is passed over the oxidation compound (10 g.). Fusion and decomposition take place at once and nitrosobenzene (1·2 g.) passes over with the steam. From the non-volatile portion there are isolated the original condensation product (2·2 g.), azoxybenzene (2 g.), and tar. A similar decomposition is brought about at lower temperatures when a solution of the oxidation compound in acetone is heated under reflux for several hours; the original condensation product is obtained in a yield of about 50%.

(c) *Action of acylating agents.* (i) A mixture of acetic anhydride (8 c.c.) and the finely powdered oxidation compound (6 g.) is maintained at 35° for several minutes, until solution is complete. After 30 minutes, crushed ice is added to the brownish-red solution and the precipitated paste is macerated with cold water until a sandy powder (3·8 g.) with the odour of nitrosobenzene is obtained. This crystallises in colourless needles, m. p. 105—106° (from dry benzene) or 99—100° (from aqueous alcohol). Yield 50%. Analysis and mixed melting-point determinations prove that it is the acetyl

derivative of the original condensation product of m. p. 136°; and it yields this on hydrolysis. A 50% yield of the same acetyl derivative is obtained by the action of acetyl chloride on a solution of the oxidation compound in pyridine.

In marked contrast to the behaviour of the original condensation product, which in pyridine solution readily gives an acetyl derivative in quantitative yield by the action of acetic anhydride, the oxidation compound is unacted upon under similar conditions at the ordinary or at a slightly raised temperature. At higher temperatures, profound decomposition sets in and unworkable tars are produced. This result clearly indicates that some prior reaction is necessary before acetylation can take place.

In a similar manner, by the action of benzoyl chloride (3 g.) on a pyridine (40 c.c.) solution of the oxidation compound (6 g.), there is obtained the benzoyl derivative of the original condensation product in 50% yield; m. p. and " mixed " m. p. 97—99°.

(d) *Action of hydrogen chloride.* Dry hydrogen chloride is rapidly absorbed by a dry ethereal solution of the oxidation compound, and an orange precipitate separates; the solution becomes colourless, but slowly turns green. If the passage of hydrogen chloride is still continued, nitrosobenzene and mesityl oxide can be isolated from the solution; but if the current is stopped when the solution becomes colourless, and the orange precipitate rapidly filtered off, washed with dry ether, and dried in a vacuum desiccator, it has the empirical formula $C_{18}H_{21}O_2N_2,2HCl$. This substance is not identical with the monohydrochloride of the original condensation product (*vide* p. 1622), but it yields this product in nearly 50% yield on treatment with water.

Action of Phenylcarbimide on the Condensation Product.—A solution of the condensation product (9 g.) and phenylcarbimide (3·3 g.; 1 mol.) in dry ether is gently warmed for 3 hours and the ether is then evaporated. The residue of colourless, cubic crystals, coated with red oil, is washed with small quantities of cold light petroleum and recrystallised from acetone, transparent, colourless cubes, m. p. 128—129° (decomp.), being thus obtained (Found: C, 71·8; H, 7·0; N, 9·7. $C_{25}H_{27}O_3N_3$ requires C, 71·8; H, 6·5; N, 10·0%). This substance is almost insoluble in cold alcohol and decomposes slightly in hot alcohol. A mixture of it with the original condensation product (m. p. 136°) melts at 104—109°.

Preparation of the Liquid Reduction Product.—To a solution of the condensation compound (60 g.) in boiling absolute ethyl alcohol (500 c.c.), sodium (23 g.) is added sufficiently quickly to keep the liquid boiling. When all the sodium has dissolved, water is added to the dark red reaction mixture and the solution is

extracted several times with ether. The ethereal solution is washed with water, extracted with dilute hydrochloric acid, and evaporated to dryness; the residue is pure azobenzene. The basic material in the acid extract is recovered and repeatedly fractionally distilled under diminished pressure, being thus separated into aniline and the new *base* (15 g.), a golden-yellow, somewhat viscous liquid, b. p. 130—133°/2—4 mm. or 160—163°/15 mm., $d_4^{15°}$ 1·0043 (Found: C, 74·8; H, 9·6; N, 7·3. $C_{12}H_{19}ON$ requires C, 74·6; H, 9·8; N, 7·25%).

Modifications of the method of reduction were tried with the object of preventing the formation of azobenzene. These included the gradual addition of sufficient acetic acid to neutralise the sodium ethoxide as it was produced—this procedure, however, caused the production of phenylcarbylamine, which was very difficult to remove on distillation. The presence of water—even 1%—in the alcohol diminishes the amount of base produced and increases the proportion of azobenzene formed even to the exclusion of the base when the quantity of water is considerable. When the absolute alcohol is replaced by amyl alcohol, no base is formed, an almost quantitative yield of azobenzene * being obtained together with a trace of aniline.

By doubling the amount of sodium used in the reduction, there was produced, in addition to the liquid base, hydrazobenzene (5 g.), which was isolated from the acid extract in the form of benzidine.

The pure base readily yields a *diacetyl* derivative, which crystallises from acetone in clusters of prismatic needles, m. p. 104—106° (Found: N, 4·9; $2CH_3{\cdot}CO$, 31·8; $1CH_3{\cdot}CO$, 19·0. $C_{16}H_{23}O_3N$ requires N, 5·05; $2CH_3{\cdot}CO$, 31·1; $1CH_3{\cdot}CO$, 15·5%). When the hydrolysis is effected by aqueous potassium hydroxide, a value for the acetyl content of 19% is quickly obtained; this value increases at only a slow rate as the heating is continued—the maximum value of 31·1% was only obtained by heating with *alcoholic* potassium hydroxide during 24 hours. It is evident, therefore, that one acetyl group is much more firmly attached than the other.

The *chloroplatinate* of the base is obtained by the addition of chloroplatinic acid (1 mol.) in alcoholic solution. The precipitate crystallises from methyl alcohol containing a small amount of hydrochloric acid in clusters of orange prisms which, after drying at 110° for 4 hours, melt and decompose at 197—198° [Found: Pt, 24·9, 24·6. $(C_{12}H_{19}ON)_2,H_2PtCl_6$ requires Pt, 24·5%].

The *nitrosoamine*, prepared by the addition of sodium nitrite to

* It is somewhat remarkable that azobenzene is reduced by sodium and boiling ethyl alcohol only with great difficulty.

a solution of the base in cold hydrochloric acid, crystallises from ether in fine, pale yellow needles, m. p. 44—48° (Found : N, 12·8. $C_{12}H_{18}O_2N_2$ requires N, 12·6%).

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BATTERSEA POLYTECHNIC, S.W. 11. [*Received, February 23rd,* 1926.]

CCXII.—*The Classification of the Sugars.*

By JOHN GWILLIAM MALTBY.

THE original classification of the normal forms of the sugars and their derivatives into the *d*- and *l*-series was that of Fischer (*Ber.*, 1894, **27**, 3208) and depended on their chemical relationship to naturally occurring (*d*-)glucose. The classification usually adopted to-day is that of Rosanoff (*J. Amer. Chem. Soc.*, 1906, **28**, 114) in which the configuration of the asymmetric group furthest removed from the aldehydic group is the deciding factor. A classification depending on the mean of the rotations of the α- and β-forms was put forward in an earlier paper (J., 1922, **121**, 2608).

Most sugars and their derivatives are obtainable in α- and β-forms, and the usually accepted distinctions between them are those given by the action of enzymes, the mode of preparation and the rate of hydrolysis of the glucosides. A different distinction has been given by Hudson (*J. Amer. Chem. Soc.*, 1909, **31**, 66) based on their rotations and on Fischer's classification into the *d*- and *l*-series. According to this, the α-form of a *d*-sugar has a more positive rotation than the β-form. In the case of arabinose, however, the two methods of distinction do not agree (Hudson, *J. Amer. Chem. Soc.*, 1924, **46**, 2591), the same being the case if Rosanoff's classification is used. It seems possible that the cause of the discrepancy lies in the classification into the *d*- and *l*-series being wrong.

It is suggested that, for the normal forms of the aldoses, the configuration of the middle group of the oxide ring (group 3) is the deciding factor in the classification into the *d*- and *l*-series. Naturally occurring arabinose therefore now belongs to the *d*- instead of to the *l*-series, and the α-forms of the *d*-sugars have more positive rotations than the β-forms for all known cases, as shown in the table below. In an earlier paper (J., 1923, **123**, 1404), it was suggested from a consideration of the rotations of the sugars

that, in the α-form of the aldoses, groups 1 and 3 have opposite configurations. It was also shown that the configuration of group 3 determines the relative proportions of the two products formed by the cyanohydrin synthesis. This follows, since the configuration of group 2 in the main product is always the opposite of that of group 4, the latter being group 3 in the original sugar. This is also shown in the table below, in which the configurations are represented by + and − signs as suggested by Fischer (*Ber.*, 1894, **27**, 3189) and the *d*-sugars have been taken as those with a positive sign for group 3.

Sugar.	Configuration of sugar.				Specific rotation of sugar.			Configuration of main cyanohydrin product.				
	5.	4.	3.	2.	α.	Equil.	β.	6.	5.	4.	3.	2.
d-Glucose	−	−	+	−	100°	52°	20°	−	−	+	−	−
d-Mannose	−	−	+	+	30	14	−15	−	−	+	+	−
d-Galactose.....	−	+	+	−	140	80	51	−	+	+	−	−
d-Arabinose ...		+	+	−	150	105	76		+	+	−	−
d-Xylose		−	+	−	92	19	−20		−	+	−	−
d-*iso*Rhamnose	−	−	+	−	73	30	—					
l-Ribose		−	−	−					−	−	−	+
l-Rhamnose ...	+	+	−	−	−7	9	54	+	+	−	−	+
l-Fucose	±	−	−	+	−112	−77	—					

KENMARE, DERBY PARK,
ROCK FERRY.

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CCXIII.—*The Unsaponifiable Matter from the Oils of Elasmobranch Fish. Part I. A Contribution to the Study of the Constitution of Squalene (Spinacene).*

By ISIDOR MORRIS HEILBRON, EDWARD DAVID KAMM, and WILLIAM MORGAN OWENS.

THE first mention of the occurrence of squalene in fish-liver oils is due to Tsujimoto (*J. Chem. Ind. Tokio*, 1906, **9**, 953), who subsequently described its physical characteristics and assigned to it the molecular formula $C_{30}H_{50}$ (*J. Ind. Eng. Chem.*, 1916, **8**, 889; 1920, **12**, 63). The hydrocarbon was found to yield a well-defined crystalline hexahydrochloride, but of indefinite melting point, sintering at about 112° and finally melting to a clear liquid at about 125°. Meanwhile, in 1915, A. Chaston Chapman, working independently, isolated from fish-liver oils obtained from Portugal what would appear to be the same hydrocarbon, for which he proposed the name spinacene, and assigned to it the same molecular formula (J., 1917, **111**, 56). Later (J., 1918, **113**, 458), from the

results of other analyses of the hexahydrochloride and hexahydrobromide and of molecular-weight determinations, he concluded that its constitution was in better accord with the formula $C_{29}H_{48}$. This author also remarked on the indefinite nature of the melting point of the hydrochloride. He found that whereas the crude compound commenced to shrink at 100° and began to melt at 110° (Cl, 33·8%),* after purification by means of benzene and alcohol, the final preparation became pasty at 120° and melted to a clear liquid at 126° (Cl, 34·5%). In a recent communication by André and Canal (*Compt. rend.*, 1925, **181**, 612), an account is given of the hydrochlorides prepared from the unsaponifiable matter of the oils of *Cetorhinus maximus* (A) and *Scymnorhinus lichia* (B). Whilst the oils from both fish had previously been examined by Tsujimoto and found to contain squalene, that from the latter has been used by us and was also almost certainly employed by Chapman (*Analyst*, May, 1917). From A, André and Canal separated two hydrochlorides: A_1, m. p. 107—108° (Cl, 35·3%, corresponding with a hydrocarbon $C_{28}H_{46}$); and A_2, m. p. 144—145° (Cl, 33·9%, indicating $C_{30}H_{50}$). On the other hand, they obtained from B the hydrochlorides B_1, m. p. 107—108° (Cl, 33·9%), and B_2, m. p. 143—145° (Cl, 33·2%), the latter chlorine content corresponding to the hydrocarbon $C_{31}H_{52}$. A mixture of A_1 and B_1 is stated to show no depression of melting point, whilst A_2 and B_2 give a slight depression (139—140°). From these highly conflicting results, the authors claim that neither squalene nor spinacene is a definite chemical compound, but each is a mixture of various unsaturated hydrocarbons from which the $C_{29}H_{48}$ homologue proposed by Chapman is apparently absent. We agree with André and Canal in so far that we have separated hydrochlorides of different melting points, but find for each *the same values* for carbon, hydrogen, and chlorine in strict agreement with a hydrocarbon formula $C_{30}H_{50}$.† It would appear that three isomeric hydrochlorides, m. p. 107—108°, 113—114°, and 144—145°, exist, although it is somewhat doubtful whether the lowest-melting one is a pure compound (see experimental part). The hydrocarbon has been regenerated from each hydrochloride and reconverted into its hydrochloride, which, in every case, is again separable into low- and high-melting fractions.

	C %.	H %.	Cl %.
* $C_{28}H_{54}Cl_6$	55·9	8·7	35·4
$C_{29}H_{54}Cl_6$	56·7	8·8	34·6
$C_{30}H_{56}Cl_6$	57·2	8·9	33·9
$C_{31}H_{58}Cl_6$	57·9	9·0	33·1

† The squalene used was obtained from *Lepidorhinus squamosus*, *Etmopterus spinax*, *Centrophorus granulosus*, and *Scymnorhinus lichia*, and the material from each source gave the same results.

TABLE I.

The Constants of Squalene.

	Chapman.	Tsujimoto.	Majima and Kubota.	Present authors.
B. p. at 0·15 mm.			205°	
0·55 ,, ...			235—237°	
2 ,, ...				240—242°
4 ,, ...				248—250°
5 ,, ...		252—254°		
9 ,, ...	260°			261—262°
10 ,, ...		262—264°		
15 ,, ...				270—275°
25 ,, ...			284—285°	
Density	$0·8610/\frac{15°}{15°}$		$0·8596/\frac{15°}{4°}$	$0·8655/\frac{13°}{13°}$
	$0·8588/\frac{20°}{20°}$	$0·8587/\frac{15°}{4°}$	$0·8584/\frac{20°}{4°}$	$0·8538/\frac{20°}{20°}$
	$0·8616/\frac{20°}{4°}$			$0·8596/\frac{18°}{18°}$
Refractive index $n_D^{15°}$ ...	1·4987		1·4959, 1·4966	
$n_D^{18°}$ ...				1·4972
$n_D^{20°}$ ...	1·4967, 1·4951	1·4965	1·4965	1·4965, 1·4980
Mol. refraction	139·1, 134·5*	139·1	139·8	139·6, 139·8, 139·9
Iodine value	367·9			377·6
Mol. wt. (cryoscopic)	394, 391 (benzene)	408 (benzene)	407 (ethylene dibromide)	391 (benzene) 439 (ethylene dibromide)

* Calculated for $C_{29}H_{48}$.

These results lead to the conclusion, which is also borne out by other evidence, that squalene and spinacene are one and the same hydrocarbon of the molecular formula $C_{30}H_{50}$. Taking into account the number of species of fish from which squalene has been isolated, we are of the opinion that no evidence has been adduced in favour of André and Canal's view (*loc. cit.*) that homologues of this hydrocarbon exist in marine animal oils. On the other hand, the isolation of the isomeric hydrochlorides would appear to indicate that squalene is itself a mixture of isomerides. In support of this view, it has repeatedly been found that the density and refractive index are not absolutely constant, although the calculated molecular refraction is almost exactly the same for different specimens. This value shows a marked exaltation ($\Sigma[R_L]_D = 1·8—2·3$) over the theoretical value for $C_{30}H_{50}|\bar{6}$. This exaltation is not due, however, to the presence, as André and Canal claim, of a $C_{31}H_{52}$ homologue in squalene, for the hydrocarbon regenerated from the hexahydrochloride melting at 107—108°, which, according to these authors, corresponds to $C_{30}H_{50}$ in the case of *Scymnorhinus lichia*, also shows exactly the same exaltation. The exaltation is apparently not due to the presence of conjugated double bonds, since we, confirming Majima and Kubota (*Jap. J. Chem.*, 1922, **1**, 9), have found that squalene is inert towards sodium and boiling amyl alcohol.

Sources of Squalene.

Squalene is widely distributed among elasmobranchs. It occurs chiefly in the family *Squalidæ*, but is not found in every member of it. Moreover, it is not peculiar to elasmobranchs, for Drummond, Channon, and Coward (*Biochem. J.*, 1925, **19**, 1047) have

reported its presence in the unsaponifiable matter of cod-liver oil. The hydrocarbon, although occurring chiefly in the liver oil, has also been found in the egg oils of *Chlamedoselachus anguineus* and *Lepidorhinus kinbei* by Tsujimoto (*loc. cit.*), and of *Etmopterus spinax*, *L. squamosus*, and *Scymnorhinus lichia* by us. Moreover, the intestines of the last-mentioned fish always contain a large amount (up to 300 c.c.) of a dark oil, the greater part of which is squalene. This may be produced *post-mortem*—the specimens when treated have always been dead for several days—but the fact that it is invariably present seems to us to favour the view that it is a characteristic of the living animal. An examination was made in May, 1925, of 115 female *E. spinax*. From some of these, eggs in a comparatively undeveloped condition were dissected, all of which contained squalene. In others, almost completely developed embryo with yolk-sac were found. The sac did not contain the hydrocarbon, which must therefore have been absorbed during the growth of the embryo. A noteworthy fact regarding squalene-containing fish is the remarkable health of their bodies, in which internal parasites are very rare (private communication from Professor Johnstone).

Decomposition of Squalene by Heat.

This has been studied by Chapman (J., 1923, **123**, 769) and Majima and Kubota (*loc. cit.*). The latter investigators subjected squalene to dry distillation and obtained fractions boiling at all temperatures from 36°/760 mm. to 235°/18 mm. They claim to have identified isoprene; the constants recorded, however, are very low ($D_4^{18°}$ 0·6692, $n_D^{18°}$ 1·39641; compare Harries, *Ber.*, 1914, **47**, 1999). From the most abundant higher fraction, a liquid, $C_{10}H_{18}$ (b. p. 62·5—66°/17 mm.), was obtained the physical constants of which resemble those of *cyclo*dihydromyrcene or *cyclo*dihydrolinolo-olene. Chapman's methods of decomposition were somewhat different, but gave apparently similar products. He concludes that the low-boiling fraction is a mixture of one or more amylenes with some isoprene or isomeric substance, whilst the main products are considered to be 1-methyl-4-propylidene*cyclo*hexane (I) and the closely related diolefinic hydrocarbon (II).

(I.) (II.)

By the dry distillation of squalene and careful fractionation of the product, we obtained members not only of the hemiterpene and monoterpene groups, but also of the sesquiterpene, diterpene, and probably even higher divisions of the same family.

The lowest-boiling liquid member obtained by us has been

definitely proved to be an amylene, oxidation of which by potassium permanganate yielded acetone, from which it follows that its structure must be $CMe_2{:}CHMe$ (III).

The fraction of next higher boiling point (62—100°/20 mm.), which appears to be a mixture of monoterpenes and dihydromonoterpenes, is under investigation.

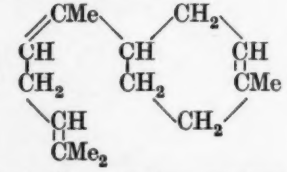
The third fraction, boiling between 120° and 170°/20 mm., consists of a complex mixture of monocyclic sesquiterpenes. By repeated distillation a constant-boiling fraction has been isolated the physical characteristics of which (Table II) are identical with those of bisabolene (Ruzicka, *Helv. Chim. Acta*, 1925, **8**, 259). In addition, ring closure by means of formic acid has yielded a dicyclic isomeride the constants of which agree closely with those of the dicyclic sesquiterpenes isolated by Ruzicka from nerolidol and which, according to this author, could only have resulted through the intermediate formation of farnesene and bisabolene (Table II).

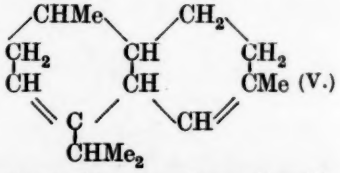
TABLE II.

	B. p./12 mm.	$d_{21°}^{21°}$.	$d_4^{21°}$.	$n_D^{21°}$.	$[R_L]_D$.
Hydrocarbon from squalene ...	129—135°	0·8734	0·8716	1·4915	67·72
Synthetic bisabolene	130—137	—	0·8717	1·4923	67·99 (Calc., 67·87)

In an attempt to obtain further evidence regarding the carbon skeleton of the entire sesquiterpene fraction, this was dehydrogenated with sulphur (compare Ruzicka, *Helv. Chim. Acta*, 1922, **5**, 345), and the product distilled over sodium. In three different experiments, addition of alcoholic picric acid produced, in insufficient quantity for analysis, orange crystals of what appeared from the melting point to be cadalene picrate. The difficulty of obtaining cadalene in appreciable quantity is not peculiar to the sesquiterpene mixture handled by us, for Staudinger (*Helv. Chim. Acta*, 1922, **5**, 785) failed to isolate any trace of this hydrocarbon on dehydrogenation of the sesquiterpene fraction from caoutchouc, which should most certainly have yielded it. Moreover, Ruzicka was unable to obtain cadalene from the compound (IV) (*Helv. Chim. Acta*, 1923, **6**, 487), whereas it was readily obtained from cadinene (V), which is similarly constituted.

(IV.)





(V.)

From the complex mixture of higher-boiling fractions dicyclic diterpenes have been isolated, and these, on treatment with formic acid, pass into tricyclic isomerides, a reaction reminiscent of the

conversion of the monocyclic α-camphorene into its tricyclic isomeride (Ruzicka, *Helv. Chim. Acta*, 1924, **7**, 279). The residue, which probably consists of members of the next higher group ($C_{25}H_{40}$), has not yet been examined.

Isomerisation of Squalene.

In addition to the isomerism due to variation in position of one or more of the ethenoid linkings, there exists, as might have been anticipated, isomerism due to ring formation. Majima and Kubota (*loc. cit.*) were the first to prove that squalene can be so isomerised, but it is apparent from their results that they failed to obtain a pure isomeride. As shown in Table III, 95% formic acid is the best catalyst for effecting ring closure in the squalene molecule, which, we have found, cannot be cyclised beyond the stage at which two double bonds remain (Table III).

TABLE III.

Molecular Refractions of Squalene Isomerides.

Isomerising agent.	Time in hours.	Ethenoid linkings (iodine values).	$[R_L]_D$. Found.	$[R_L]_D$. Calc.	$\Sigma[R_L]_D$.
(Pure squalene)	—	6	139·8	137·98	1·85
Acetic anhydride with sulphuric acid	2½	—	136·9	—	—
Alcoholic sulphuric acid ...	18	—	134·0	—	—
Formic acid	½	—	136·9	—	—
„ „	3	3	134·3	132·6	1·7
„ „	9	3	134·1	132·6	1·5
„ „	24 (or longer)	2	133·2	130·9	2·3

Constitution of Squalene.

At this point we would again emphasise our conviction that squalene and spinacene are identical. In addition to the evidence of the hydrochloride formation, we are led to this conclusion by the following considerations:

(*a*) The physical properties of spinacene as recorded by Chapman agree closely with those recorded by all other workers in the same field (Table I).

(*b*) The calculated molecular refraction for $C_{29}H_{48}|\bar{6}$ is 133·1, not 134·3 as stated by Chapman (J., 1918, **113**, 458). The value of 134·5 determined by him is in no better agreement with this than the value worked out from the same data for $C_{30}H_{50}|\bar{6}$ (139·3) is with the theoretical value 137·7.

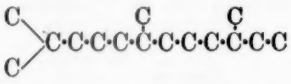
(*c*) It does not appear to us that evidence based on cryoscopic measurements can be considered sufficiently trustworthy to distinguish between successive homologues ($C_{29}H_{48}$,$C_{30}H_{50}$) of such high molecular weight.

(*d*) The recorded chemical properties of squalene and spinacene are identical.

The constitution of spinacene (VI) tentatively proposed by Chapman will therefore not be discussed, not only because of the difficulty of accepting the $C_{29}H_{48}$ molecular formula, but because it fails to account for the formation of the typical terpene products above mentioned.

(VI.)
$$\begin{array}{l} CH_2Me\cdot CH{:}CMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH{:}CH\cdot CMe{:}CH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2Me\cdot CH{:}CMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH{:}CH\cdot CMe{:}CH \end{array}$$

That squalene is a terpene compound is evidenced by the ease with which it undergoes ring closure, by its ready regeneration from the hexahydrochloride, and by the large quantities of succinic and lævulic acids obtained on decomposition of its ozonide (Majima and Kubota, *loc. cit.*). The isolation of bisabolene proves that at least one-half of the squalene molecule must have the carbon skeleton



and the fact that diterpenes have also been obtained indicates that, as suggested by Majima and Kubota, the hydrocarbon is a dihydrotriterpene. We do not agree, however, with the structure (VII) postulated by these authors, which fails to show the complete relationship of squalene to terpene hydrocarbons in general, but consider that squalene is an equilibrium mixture of isomerides, one form of which might be represented by (VIII).

(VII.)
$$\left.\begin{array}{l} CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CH_2\cdot CH_2\cdot CH{:}CH \\ CH_2{:}CMe\cdot CH_2\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH_2\cdot CH{:}CH \end{array}\right\rangle C_6H_{12}$$

(VIII.) $CMe_2{:}CH\cdot CH_2\cdot[CH_2\cdot CMe{:}CH\cdot CH_2]_4\cdot CH_2\cdot CMe{:}CHMe$

Table IV shows that, as is to be anticipated from formula (VIII), the closest analogy exists between the products of decomposition of squalene and caoutchouc (Staudinger and Fritschi, *Helv. Chim. Acta*, 1922, **5**, 785).

Significance of Squalene.

That squalene is intimately connected with metabolic processes is self-evident, and in this connexion we desire to direct attention to a possible relationship between this hydrocarbon, stigmasterol ($C_{30}H_{50}O$), and cholesterol ($C_{27}H_{46}O$).* Feeding experiments carried out on rats by Mr. H. J. Channon, of University College, London,

* [Note added, June 18th.] Attention is also directed to the recent paper of Oikawa (*J. Biochem.* [*Japan*], 1925, **5**, 63), the abstract of which has just appeared, in which the isolation from shark bile of a pentahydric alcohol, $C_{27}H_{48}O_5,2H_2O$, is reported.

show that the administration of squalene results in the amount of cholesterol in the liver being more than doubled. This observation may support the view that squalene is a precursor in cholesterol synthesis in the animal body; on the other hand, the large cholesterol increase may be due to some factor yet to be determined. Further biochemical work is in progress to confirm or disprove the hypothesis.

TABLE IV.

Comparison of the Products of Decomposition of Squalene and Caoutchouc.

Product.	Source.	*M.*	B. p.	*d*.	n_D.	$[R_L]_D$.	$[R_L]_D$ calc. for
C_5H_8	Caoutchouc		30—50°/760 mm.				
C_5H_{10}	Squalene		32—40°/760 mm.				
$C_{10}H_{16}$	Caoutchouc	142	58°/11 mm.	0·8390/20°	1·4724/20°	45·42	$C_{10}H_{16}$ = 45·24
	Squalene (cyclised by HCO_2H)		86—101°/25 mm.	0·8326/21°	1·465/21°	45·17	
$C_{15}H_{24}$	Caoutchouc	200	88—91°/0·05 mm.	0·8895/20°	1·4980/20°	67·23	$C_{15}H_{24}$ = 67·83
	Squalene		129—135°/12 mm.	0·8734/21°	1·4915/21°	67·8	
			152—162°/15 mm.	0·8934/16°	1·499/16°	67·04	
$C_{30}H_{52}$	Caoutchouc	268	118—122°/0·02 mm.	0·9046/20°	1·5063/20°	89·41	$C_{30}H_{52}$ = 88·7
	Squalene		180—190°/9 mm.	0·9073/19°	1·5080/19°	89·33	
		259	190—200°/9 mm.	0·9157/19°	1·513/19°	88·88	
—	Caoutchouc	303	142—148°/0·04 mm.	0·9161/20°	1·5119/20°	89·17 (if $C_{20}H_{32}$)	$C_{25}H_{40}$ = 111·3
						111·2 (if $C_{25}H_{40}$)	

EXPERIMENTAL.

Extraction of Oils.—The fish were dissected immediately on arrival, and the livers removed and weighed. The stomach was in each case ligatured and the contents were examined for the presence of oil. Any eggs in the females were separated and examined. Table V gives the oil content of the various species. The livers were cut into small pieces and the oil was extracted by heating with a coil into which steam was admitted for about ½ hour. The liberated oil was separated from tissue matter by means of a centrifuge and was obtained as a clear mobile liquid, pale yellow to orange in colour.

Extraction of the Hydrocarbon from the Liver Oil.—(a) *Saponification.* Considerable difficulty was experienced in saponifying the oil and separating the unsaponifiable matter. After many experiments, including saponifications in alcohol, it was found that the most satisfactory method was to heat the oil (500 c.c.) in a nickel basin to 105—110° and add drop by drop an equal volume of 20% sodium hydroxide solution with continuous stirring. After saponification was complete (about 1 hour), sodium chloride (150 g.) was added together with 150 c.c. of hot water. The mixture when cool was filtered through cloth, and the oil was separated from the aqueous layer, dried over sodium sulphate, and distilled at 3 mm. pressure. The squalene so obtained had a refractive index of about 1·497 and contained a small quantity of oxygenated substance (compare Chapman, J., 1917, **111**, 56).

TABLE V.

Measurements of Fish and Yield of Oil.

Fish.	Date.	No.	Sex and condition.	Length (cm.).	Wt. (g.).	Wt. of liver (g.).	Liver oil (c.c.).	Stomach oil (c.c.).	Squalene in liver oil (%).
Scymnorhinus lichia.	12.3.24	1		113	7190	1530	2000	200	
		1		112	6270	1542			
	8.5.25	1	Male.	101	4550	840	800	150	Average = 55
	12.5.25	1	Male.	125	—	2230	2000	250	
	20.5.25	5	Males.	Average = 110	—	—	1230	130	
		1	Female.	100	—	—	1000	100	
Etmopterus spinax.	11.5.25	115	Mature females.	Average = 23	108	30	18	—	50
Centrophorus granulosus.	29.5.25	1	Female (after spawning).	131	—	2950	2500	—	80
Lepidorhinus squamosus.	1.11.24	1	Mature female.	125	—	3800	3000	—	65
		1	Female (after spawning).	123	—	1800	1500	—	
	1.5.25	5	Males.	Average = 109	—	1570	750	—	74

(b) *Distillation Method.*—This method (compare Tsujimoto, *loc. cit.*) is more rapid than the preceding for the preparation of large quantities of the hydrocarbon. The oil (in portions of not more than 200 g.) was distilled under 3 mm. pressure; no distillate appeared below 235°, the major portion distilling regularly between 240° and 250°. Distillation was stopped as soon as the first signs of fuming were noticed, and an oil, containing as chief impurity a small quantity of free fatty acid, was thus obtained ($n_D^{20°}$ 1·497—1·498). It was dissolved in ether, the solution, after being washed several times with dilute sodium hydroxide solution and finally with water, was dried over calcium chloride, the ether removed, and the residual oil distilled. The products ($n_D^{20°}$ 1·498) thus obtained from different samples, as in the previous case, contained varying quantities of oxygen (C, 87·4, 87·2; H, 11·9, 12·0%). Pure squalene can, however, be obtained from them (*a*) through the hydrochloride, (*b*) by treatment with phthalic anhydride.

The crude hydrocarbon (160 g.) was heated for 5 hours with phthalic anhydride (18 g.) at 130—140°. After cooling and removal of unchanged anhydride, the oil in ethereal solution was shaken successively with dilute sodium carbonate and sodium hydroxide solution and washed with water. The ether was removed from the dried solution, and the residual oil distilled, the whole coming over at 260—262°/9 mm.; $n_D^{18°}$ 1·4982, $n_D^{20°}$ 1·4965, $d_{18°}^{18°}$ 0·8596; $[R_L]_D$ 139·6 (Found: C, 87·7, 87·7; H, 12·1, 12·0. $C_{30}H_{50}$ requires C, 87·8; H, 12·2%).

The sodium carbonate washings contained no acid phthalate, and it must be concluded that the impurity present in the crude hydrocarbon is either a tertiary alcohol, which would seem to be closely related to the hydrocarbon, or an internal oxide similar in nature to cineole, which compound on treatment with dehydrating agents readily passes into dipentene. This point is being further examined.

Treatment of crude squalene with acetic anhydride and *d*-cam-

phorsulphonic acid also removes the impurity as a lower-boiling liquid of sharp odour. This method, however, cannot be used for the preparation of squalene, because isomerisation also occurs.

Squalene Hexahydrochloride. General Method of Preparation.—Dry acetone (15 g.) was saturated with dry hydrogen chloride at −5° and squalene (5 g.) was added, the stream of gas being continued until the whole became solid; the colour of the solution changed through red to almost black. The resulting hydrochloride (6 g.) was washed free from coloured oily impurity with dry ether. By keeping the filtrate, again saturated with hydrogen chloride, in the ice-chest, a further small crop was obtained (approx. 3%). If the acetone is not presaturated with hydrogen chloride, the first crop obtained is very much smaller; the total yield, however, is only slightly diminished, as a large crop separates during the second treatment. This method is much slower and generally less satisfactory than the first. Ether also can be employed as solvent, but cannot be relied upon to give such consistent yields, being apparently sensitive to minute alteration of conditions. Analysis of the washed crude hydrochloride from any of the sources examined by us always gave similar analytical values (*e.g.*, found: C, 57·1, 57·0; H, 9·0, 8·8%). The hydrochloride can be prepared equally readily from squalene-containing oils.

Separation of the Isomerides. Isolation of the 107—108° *Hydrochloride from Squalene obtained from* Scymnorhinus lichia.—The crude hydrochloride (14 g.), m. p. 109—112°, was digested with dry acetone (300 c.c.) for 10 minutes at 50°, boiled for one minute, and the residue (2·4 g.) filtered off. The filtrate on standing deposited hydrochloride (9·2 g.) which melted at 107—108° (Found: C, 57·2, 57·2; H, 8·8, 9·1; Cl, 33·6%). The yields of this compound, which was not always produced, varied widely even when the conditions were precisely similar. Although it appeared to be a definite isomeride, nevertheless, on digestion with hot acetone, a small residue (m. p. 111—122°) was invariably obtained.

Isolation of the High-melting Isomeride.—The residue (m. p. 126—130°) obtained above was combined with other sparingly soluble fractions which had been worked up in the same way. The total material (6 g.) was boiled with acetone (175 c.c.), which was then filtered quickly. The undissolved solid (2·3 g.), m. p. 140—142°, was again similarly treated with acetone (250 c.c.), and the residue (1·7 g.), now melting at about 144°, recrystallised from ethyl acetate. It formed characteristic rhombic plates, m. p. 144—145°, very similar in appearance to the 107—108° isomeride, and was practically insoluble in acetone or alcohol and moderately easily soluble in ethyl acetate (Found: C, 56·9, 56·8; H, 8·9, 8·8; Cl, 33·6, 33·8%). The intermediate portions obtained from the filtrates melted in-

definitely between 111° and 120° and were separated into the high-melting hydrochloride and an isomeride, m. p. 113—114°.

The latter compound was readily prepared as follows: The washed crude hydrochloride (36 g.) was recrystallised from ethyl acetate (270 c.c.), and the separated solid (32 g., m. p. 111—120°) digested with boiling ethyl acetate. The insoluble residue (11 g., m. p. 117—130°) was now taken up in hot acetone and separated from 5 g. of undissolved material (m. p. 131—137°) by filtration. From the filtrate, crystals, m. p. 113—114°, were obtained. This compound showed no alteration in melting point on further crystallisation from acetone, in which it is moderately easily soluble, although less so than the 107—108° form (Found: C, 56·8; H, 8·9; Cl, 33·8, 33·9%).

Regeneration of Squalene from the Hydrochlorides.—(A) 113—114° *Isomeride.* The hydrochloride (17 g.) was boiled under reflux with pyridine (68 g.) for 4 hours in an atmosphere of carbon dioxide. The reaction mixture was poured into an excess of dilute sulphuric acid, and the hydrocarbon extracted with ether. The ethereal solution was well washed with water, dried, and, after removal of the solvent, the residual oil was distilled at 4 mm. The constant-boiling fraction was again redistilled at the same pressure, and the major portion, boiling at 240—242°, collected separately, $n_D^{20°}$ 1·4990, $d_{20°}^{20°}$ 0·8592, $[R_L]_D$ 140·2, $[R_L]_D$ calc. for $C_{30}H_{50}|\bar{6}$ 137·7 (Found: C, 87·8, 87·5; H, 12·1, 12·2. $C_{30}H_{50}$ requires C, 87·8; H, 12·2%). The regeneration can also be brought about with alcoholic sodium ethoxide, silver acetate, or quinoline. Even prolonged boiling with absolute alcohol is sufficient to effect complete decomposition of the hydrochloride.

(B) 107—108° *Isomeride.* This was similarly decomposed and the constants of the pure hydrocarbon were determined, $n_D^{20°}$ 1·4955, $d_{20°}^{20°}$ 0·8563, $[R_L]_D$ 139·8 (Found: C, 87·6, 87·7; H, 12·3, 12·3%).

(C) 144—145° *Isomeride.* This proved slightly more difficult to decompose. The constants of the hydrocarbon after distillation over sodium were: $n_D^{16·5°}$ 1·4990, $d_{16·5°}^{16·5°}$ 0·8612, $[R_L]_D$ 139·8 (Found: C, 87·4; H, 12·2%).

Regeneration of the Hydrochlorides.—Each of the regenerated hydrocarbons was converted into the hydrochlorides in the usual way and these, on treatment with acetone as previously described, were separated into high- and low-melting components.

Treatment of the Oily Residues.—After removal of the major portions of the hydrochloride, the acetone and ethyl acetate mother-liquors invariably yielded, on concentration, successive crops of lower-melting compounds (*e.g.*, 95—96°, 84°, and 69°) and finally a sparingly soluble oil separated. That this consisted of partly decomposed hydrochloride was shown by again saturating it with

hydrogen chloride, when, on standing at 0°, the usual mixture of isomerides (m. p. 110—116°) was again produced (Found : C, 57·0, 57·1; H, 8·9, 8·9%).

Squalene Hexahydrobromide.—Tsujimoto (*loc. cit.*) gives m. p. 115—126° for this compound, whilst Chapman states that, after three crystallisations from benzene, it softens at 126° and melts to a clear liquid at about 132°. Provided that the two compounds are identical, a similar discrepancy occurs in the analytical values, the results obtained by the former (C, 40·2; H, 6·4; Br, 53·0, 53·5%) being in good accord with $C_{30}H_{50}$, whilst Chapman's result (Br, 54·5%) agrees with $C_{29}H_{48}$. We have prepared this compound by the usual method (5 g. of squalene) and obtained it by recrystallisation from hot acetone in lustrous plates melting at 118—120° to a clear liquid. Although this compound has not been prepared in large quantity, a sufficient examination has been made to show that higher-melting isomerides can be obtained. The m. p. of a specimen that had been kept for 2 months in a desiccator over solid sodium hydroxide fell to 110—113°, doubtless owing to partial decomposition (Found : C, 40·1; H, 6·3; Br, 53·5, 53·7. $C_{30}H_{56}Br_6$ requires C, 40·2; H, 6·3; Br, 53·5%).

Isomerisation.—(a) *Acetic anhydride containing sulphuric acid.* Squalene (150 g.) was boiled under reflux for 2½ hours with acetic anhydride (200 c.c.) containing 2 c.c. of sulphuric acid. The product was poured into water, neutralised with sodium carbonate, and extracted with ether. After removal of solvent from the dried solution, distillation of the residue yielded a pale yellow oil, b. p. 253—256°/4 mm., $n_D^{20°}$ 1·5080, $d_4^{20°}$ 0·8939, $[R_L]_D$ 136·7.

(b) *Alcoholic sulphuric acid.* Squalene (10 g.) was boiled under reflux with 50 c.c. of alcoholic sulphuric acid (15% H_2SO_4) for 2 days. The product, after extraction as above, gave on distillation a main fraction, b. p. 235—240°/3 mm., $n_D^{15°}$ 1·5049, $d_{15°}^{15°}$ 0·9073, $[R_L]_D$ 134·01.

(c) *Formic acid.* The hydrocarbon was boiled under reflux with twice its weight of formic acid (98%) for various periods. After cooling, the solution was diluted with water and treated as above. The products were :

Reaction period, ½ hour.—Mobile, pale yellow oil, b. p. 215—225°/2 mm., $n_D^{18°}$ 1·5060, $d_{15°}^{15°}$ 0·8900, $[R_L]_D$ 136·8.

Reaction period, 3 hours.—Rather viscous, pale yellow oil, b. p. 232—233°/3 mm., $n_D^{15°}$ 1·5150, $d_{15°}^{15°}$ 0·9207, $[R_L]_D$ 134·3, iodine value 179·9 ($C_{30}H_{50}|_3^-$ requires iodine value 185·8, $[R_L]_D$ 132·6).

Reaction period, 24 hours to 3 days.—Very viscous, pale yellow oil, b. p. 230—232°/3 mm., $n_D^{15°}$ 1·5211, $d_{15°}^{15°}$ 0·9359, $[R_L]_D$ 133·2, iodine value 117·4 ($C_{30}H_{50}|_2^-$ requires iodine value 124·6, $[R_L]_D$ 130·9).

It will be seen that the isomerisation occurs in stages. On the assumption, which seems likely from the final results, that the

exaltation of the molecular refraction persists throughout, the product of ½ hour's treatment contains two rings, that of 3 hours' treatment, three rings, whilst the maximum ring closure (four) is reached after 3 days, when only two double bonds remain. For each ring formed, an increase in density and in viscosity occurs; the final product has the consistency of thick treacle, only pouring with difficulty from a test-tube at room temperature.

Attempted Reduction of Squalene by Sodium and Amyl Alcohol.—A mixture containing squalene (5 g.), sodium (10 g.), and amyl alcohol (20 g.) was heated to boiling, and to this, amyl alcohol was added drop by drop until all the sodium had dissolved. After treatment with water, and extraction with ether, the whole was distilled; unchanged squalene was then recovered ($n_D^{13°}$ 1·5022, $d_{13°}^{13°}$ 0·8655, $[R_L]_D$ 139·85). The reaction was repeated with *n*-octyl alcohol, with the same result.

Dry Distillation of Squalene.—Squalene (700 g.) was distilled, in portions of not more than 150 c.c., from a 250 c.c. flask through an air condenser into another distillation flask, which served as a receiver for all high-boiling liquid. The side tube of this receiver was connected to a spiral of glass tube immersed in a freezing mixture of ice and salt, which effectively condensed the low-boiling products of the reaction. The outlet of this spiral was connected to an absorption bottle containing a 10% solution of bromine in chloroform.

During the distillation, no appreciable absorption took place, although a small quantity of a combustible gas passed through the bromine solution. The total distillate amounted to about 600 g., the residue being a polymerised resin.

The distillate was separated by fractionation into five main portions:

	B. p.	Pressure.	Wt.		B. p.	Pressure.	Wt.
1.	30— 45°	760 mm.	36 g.	4.	170—20°	115 mm.	110 g.
2.	60—100	20 ,,	224 ,,	5.	210—240	15 ,,	65 ,,
3.	120—170	20 ,,	137 ,,				

Fraction 1 was refractionated at atmospheric pressure, yielding (*a*) 28 g., b. p. 32—40°, $n_D^{20°}$ 1·3940; (*b*) 2 g., b. p. 55—75°, $n_D^{20°}$ 1·4290; (*c*) 4 g., b. p. above 75°, $n_D^{20°}$ 1·4615.

20 G. of (*a*) (which was not further divisible by fractional distillation) were dissolved in cold dry carbon disulphide and treated with a 10% solution of bromine in the same solvent until the colour of the bromine just persisted after vigorous shaking and standing. After removal of carbon disulphide, the residue was distilled, and the fraction, b. p. 80—100°/20 mm., collected (yield, 35 g.). After several fractionations, a colourless liquid was obtained as the main portion, having b. p. 65—67°/13 mm., $n_D^{19°}$ 1·5140, $d_{19°}^{19°}$ 1·6773, $[R_L]_D$ 41·29 (Found: Br, by the Carius method, 72·1. $C_5H_{10}Br_2$ requires Br, 69·6%; $[R_L]_D$ 40·84).

In order to satisfy ourselves that under precisely similar conditions isoprene yields the tetrabromo-derivative, we brominated this hydrocarbon. The product was a heavy, yellow oil, b. p. 152—156°/12 mm., $n_D^{20°}$ 1·5978, agreeing well with previously reported values for isoprene tetrabromide (Staudinger, *Helv. Chim. Acta*, 1922, **5**, 765, gives b. p. 153—155°/12 mm.). Since in the case under consideration a dibromide only was formed, it is obvious that the low-boiling distillate was either a single amylene or a mixture of isomerides.

Oxidation of the amylene. 9 G. were shaken with a slight excess of 2½% potassium permanganate solution (23 g. $KMnO_4$). After treatment with sodium bisulphite, the solution was filtered and fractionally distilled through a long column. The first 60 c.c. of the distillate were treated with *p*-nitrophenylhydrazine in hydrochloric acid and, after 12 hours, the precipitate produced was twice crystallised from dilute aqueous alcohol; yellow crystals of acetone-*p*-nitrophenylhydrazone (m. p. and "mixed" m. p. 146°) were thus obtained.

Fraction 3 (b. p. 120—170°/20 mm.). This was distilled at 15 mm. and separated into the following fractions: (A) b. p. 110—122°, 16 g.; (B) b. p. 122—134°, 29 g.; (C) b. p. 134—144°, 40 g.; (D) b. p. 152—162°, 26 g.; (E) viscous residue.

(A) was apparently a mixture of mono- and sesqui-terpenes ($n_D^{18°}$ 1·4782, $d_{4°}^{18°}$ 0·8459). Cyclisation by boiling with 98% formic acid (30 g.) for 3 hours yielded an oil which was distilled at 25 mm. into two main fractions: (1) 5 g., b. p. 86—100°, $d_{21°}^{21°}$ 0·8326, $n_D^{21°}$ 1·4560, $[R_L]_D$ 45·17 (calc. for $C_{10}H_{16}|\bar{2}$, 45·2). (2) 8 g., b. p. 130—140°, $n_D^{20°}$ 1·4850.

(1) was a colourless mobile oil with an odour closely resembling that of pinene. (2) was added to sub-fraction B, which, however, further distillation indicated to be an inseparable mixture and was not further examined.

Sub-fraction C was distilled over sodium and yielded as major portion a faintly greenish-yellow oil, b. p. 129—135°/12 mm., $n_D^{21°}$ 1·4915, $d_{21°}^{21°}$ 0·8734, $d_{4°}^{21°}$ 0·8716, $[R_L]_D$ 67·7 (calc. for $C_{15}H_{24}|\bar{3}$, 67·8). These constants are identical with those of bisabolene (Table III) (Found: C, 87·9, 87·6; H, 11·6, 11·8. Calc. for $C_{15}H_{24}$: C, 88·2; H, 11·8%).

20 G. of this substance were cyclised by boiling with 98% formic acid (40 g.) for 3 hours, and the product was distilled at 21 mm. and separated into: (1) 2 g., b. p. 132—135°, $n_D^{20°}$ 1·4870; (2) 1 g., b. p. 137—145°, $n_D^{20°}$ 1·4912; (3) 14 g., b. p. 140—145°, $n_D^{20°}$ 1·4965, $d_{20°}^{20°}$ 0·8994, $[R_L]_D$ 66·28 (calc. for $C_{15}H_{24}|\bar{2}$, 66·1).

The main fraction would appear to be very similar to one of the hydrocarbons obtained by Ruzicka (*loc. cit.*) by treating nerolidol with formic acid, the constants for which were b. p. 114—116°/12 mm., $d_{4°}^{20°}$ 0·9069, $n_D^{20°}$ 1·4964, $[R_L]_D$ 65·82.

The whole of (3) was heated with finely-powdered sulphur (5 g.) at 200—250° until no more hydrogen sulphide or mercaptan was evolved (16 hours). The volatile products of the reaction (4 g.) were distilled in a vacuum from the large amount of resinous matter produced, repeatedly distilled over sodium until colourless, and treated with a concentrated hot alcoholic solution of picric acid. After 12 hours, the deposited red oil was redissolved in alcohol. In the solution, after several weeks, there suddenly appeared yellow laminæ of picric acid mixed with long orange needles, which were mechanically separated. These commenced to shrink at 95° and melted to a clear red liquid at 108—111° (cadalene picrate has m. p. 114—115°). Similar treatment of somewhat less highly fractionated sesquiterpene products gave, on two occasions, the same orange crystals, but sufficient pure material has not yet been collected for mixed melting-point determinations with cadalene picrate.

Sub-fraction D was a somewhat more viscous and more deeply coloured oil. The constants $n_D^{16°}$ 1·4990 and $d_{16°}^{16°}$ 0·8934 and the impossibility of obtaining constant-boiling fractions on redistillation indicate that it is a mixture containing a large proportion of the next fraction.

Fraction 4 (b. p. 170—210°/15 mm.). 20 G., on fractional distillation at 9 mm., gave: (A) 8 g., b. p. 180—190°, $d_{19°}^{19°}$ 0·9073, $n_D^{19°}$ 1·5082, $[R_L]_D$ 89·39 (Found: C, 87·8; H, 11·6); (B) 6 g., b. p. 190—200°, $d_{19°}^{19°}$ 0·9157, $n_D^{19°}$ 1·5130, $[R_L]_D$ 88·88 (Found: C, 88·0; H, 11·7; *M*, cryoscopic in benzene, 259. Calc. for $C_{20}H_{32}$: C, 88·2; H, 11·8%; *M*, 272. $C_{20}H_{32}|\bar{3}$ and $C_{20}H_{32}|\bar{4}$ require $[R_L]_D$ 88·76 and 90·46, respectively).

Both (A) and (B) were greenish-brown, rather viscous, and almost odourless oils. The latter seems to be identical with the compound of molecular weight 303, obtained by Staudinger (*loc. cit.*) by the distillation of caoutchouc, and assumed by him to be $C_{25}H_{40}|\bar{4}$ (see Table IV).

Treatment of (B) with boiling formic acid for 3 hours gave an isomeride, b. p. 190—200°/9 mm., $d_{20°}^{20°}$ 0·9258, $n_D^{20°}$ 1·5090, $[R_L]_D$ 87·72 (calc. for $C_{20}H_{32}|\bar{2}$, 87·1).

Fraction 5 was a dark-coloured, viscous oil which awaits detailed examination.

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